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Volume 8



1944

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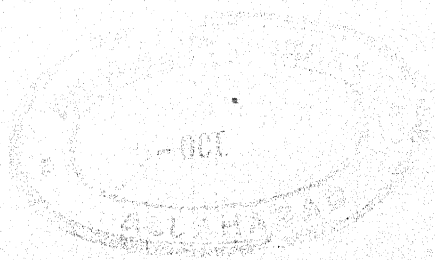
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Sie, sie bleibt die Natur, und wenn auch hier
alles verwelket,
Wenn auch hier alles der Zeit brausender
Wirbel verschlingt;
Wenn er, wie Blätter ein Bach, das Leben der
Völker dahinreißt,
Leicht ihre Formen zerbricht, und über
Leichen sich wälzt —
Bleibt sie doch die Natur, es grünt ihr am
Busen die Flora,
Und in ätherischer Luft glüht sie am ewi-
gen Eis;
Lächelnd sieht sie herab auf der Nationen
Umwälzung,
Und die Brandung der Welt thürmt nicht
die Wogen zu ihr.
Staaten mögen verblühen, die Rose der Alpen
blüht ruhig
In des Urgebirgs Schooss, ruhig das Veil-
chen im Thal,
Anemonen, Ranunkeln, Dryaden, und Primel
und Steinbrech
Leben am Berge stets fort, Kinder der gros-
sen Natur,
Und im Thale da steh'n Hyacinthen, Narcis-
sen und Sinngrün,
Scherzend am silbernen Quell freut das
Vergissmeinnicht sich.
Menschen, ehrt die Natur! umarmt die Mut-
ter der Blumen,
Dann hört auch sie euch dereinst, wenn
ihr Vergissmeinnicht ruft.

SUTER, Flora Helvetica I (1802)

98254

• Chronica Botanica, Volume 8, Number 1 •

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38

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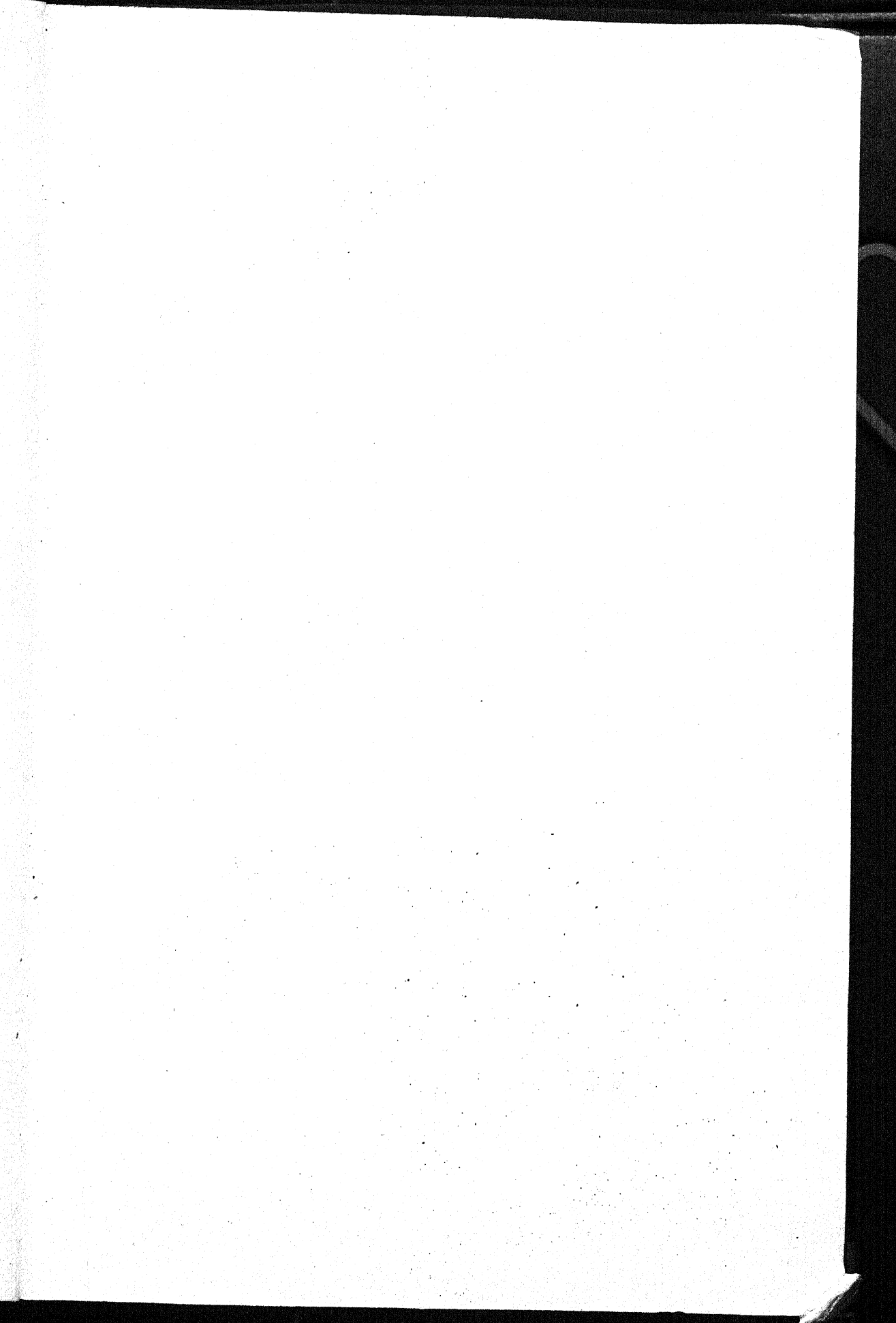
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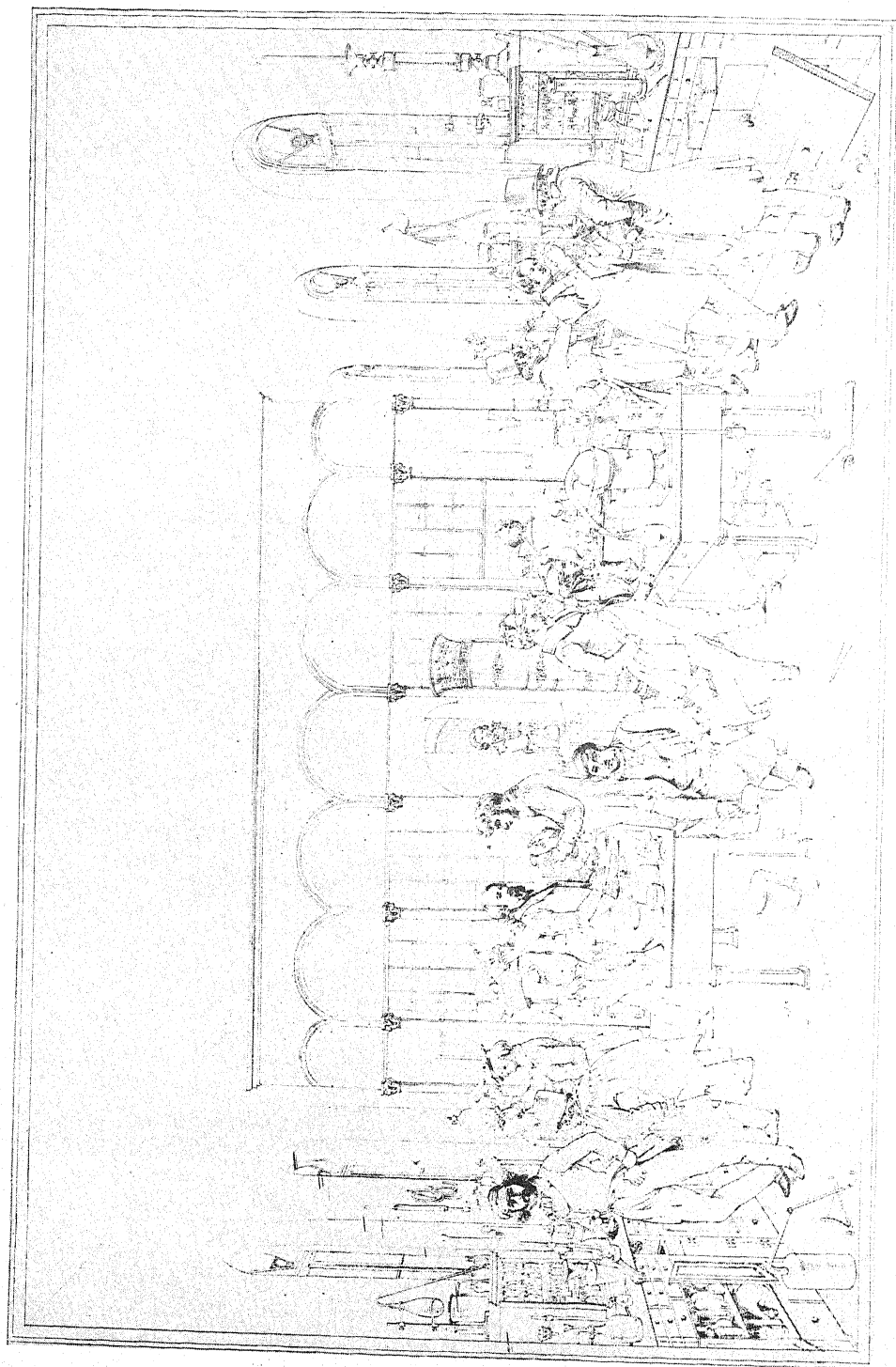
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Justus von Liebig—man and teacher. Liebig and the law of the minimum. Amer. Assoc. Adv. Science Monograph 16, "Liebig and After Liebig—A Century of Progress in Agricultural Chemistry": 1-9, 71-82. 1942.

CHARLES ALBERT BROWNE was born, August 12, 1870, in North Adams, Massachusetts. A.B., 1892, A.M., 1894, Hon. Sc.D., 1924, Williams College. A.M., Ph.D., Goettingen, 1902. Hon. Sc.D., Stevens Inst. Technology, 1925. Chemical Analyst, New York City, 1892-1894. Instructor in chemistry, Penn. State Coll., 1895-1896. Asst. Chem., Penn. Agr. Expt. Station, 1896-1900. Studied Chemistry, Agriculture, and Plant Physiology at Goettingen, 1900-1902. Research Chemist, La. Agr. Expt. Station, New Orleans, 1902-1906. Chief, Sugar Laboratory, U. S. Bur. Chemistry, 1906-1907. Chemist in Charge, N. Y. Sugar Trade Laboratory, 1907-1923. Chief, U. S. Bur. Chemistry, 1923-1927. Chief, Chem. and Tech. Research, U. S. Bur. Chemistry and Soils, 1927-1935. Supervisor, Agr. Chemical Research, U. S. Bur. Agr. and Eng. Chem., 1935-1940. Retired 1940. Editor, Golden Jubilee Number of Amer. Chem. Soc., 1926. Pres., Assoc. Off. Agr. Chemists, 1924-1925. Pres., History of Science Soc., 1935-1936. Hon. mem., Am. Oil Chem. Soc.; Hon. fellow, Sugar Tech. Assoc. of India. Gold and silver medals for agr. chem. exhibits, St. Louis Expos., 1904. Award of distinction, Assoc. Grocery Manufacturers of Amer. for applications of science to food production. U. S. delegate 6th Internat. Cong. Applied Chem., Rome, 1906; Internat. Soc. Sugar Cane Technologists, Brisbane, 1935. Nicholas Appert Medal Award of the Institute of Food Technologists for 1944.





Lübig's Laboratory at Gießen. — Interior view from an old print of a drawing by Trautschold in 1842

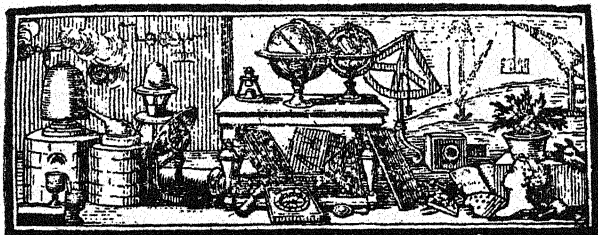
A SOURCE BOOK of AGRICULTURAL CHEMISTRY

by

CHARLES A. BROWNE

Bureau of Agricultural and Industrial Chemistry,
U. S. Department of Agriculture

"The ascent of the Sap, the Distribution of the Aer, the Confection of several sorts of Liquors, as Lymphas, Milks, Oyls, Balsames; with other parts of Vegetation, are all contrived and brought about in a Mechanical Way. In sum, Your Majesty will find, that we are come ashore into a new World, whereof we see no end."
(NEHEMIAH GREW's dedication of his "Anatomy of Plants," 1682, to King Charles II).



CONTENTS

PREFACE	VI
INTRODUCTION — <i>Agricultural Chemistry Defined</i>	VIII

Chapter I

AGRICULTURAL CHEMISTRY IN ANCIENT TIMES:

<i>Theories</i> — EARLY GREEK NATURE PHILOSOPHERS (THALES, ANAXIMENES, HERACLITUS, EMPEDOCLES, ANAXAGORAS) — DEMOCRITUS — ARISTOTLE — EXPERIMENTAL SCIENCE IN THE LATER GREEK EPOCH (HERON) — <i>Practices</i> — CAIUS PLINIUS SECUNDUS (SOILS, FERTILIZERS, AGRICULTURAL TECHNOLOGY, AGRICULTURAL ANALYSIS) — <i>Relations of Medicine and Pharmacy to Agricultural Chemistry</i> — DIOSCORIDES	1
--	---

Chapter II

AGRICULTURAL CHEMISTRY IN THE ALCHEMICAL AND IATROCHEMICAL PERIODS: PARACEL-

SUS — PALISSY — DUCHESNE — BACON — SALA — VAN HELMONT — GLAUBER — PLATTES	22
---	----

Chapter III

AGRICULTURAL CHEMISTRY IN THE TIME OF THE EARLY ROYAL SOCIETY: BOYLE — REDI —

HOOKE — MAYOW — GREW — WINTHROP, THE YOUNGER — CLAYTON — WOODWARD — HALES — TULL	54
--	----

Chapter IV

AGRICULTURAL CHEMISTRY IN THE EARLY PHLOGISTON PERIOD: BECHER — STAHL — BOERHAAVE

— RÉAUMUR — DUHAMEL — MARGGRAF — HOME — WALLERIUS	97
---	----

Chapter V

AGRICULTURAL CHEMISTRY IN THE LATE PHLOGISTON PERIOD: BLACK — PRIESTLEY — INGEN-

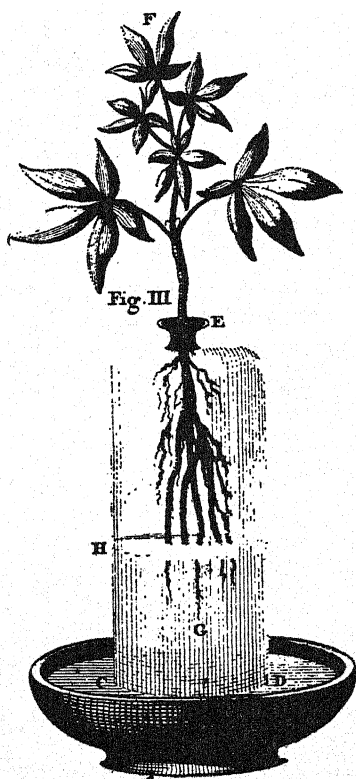
HOUSZ — SENEBIER — CAVENDISH — SCHEELÉ	135
--	-----

Chapter VI

AGRICULTURAL CHEMISTRY DURING THE CHEMICAL REVOLUTION: LAVOISIER — THAER AND EINHOF	
— CHAPTAL — HERMBSTÄDT — DE SAUSSURE — DAVY — DE	
CANDOLLE	164

Chapter VII

AGRICULTURAL CHEMISTRY AT THE BEGINNING OF THE MODERN PERIOD: WIEGMANN — SCHÜBLER —	
SPRENGEL — BOUSSINGAULT — MULDER — LIEBIG	
	220
SUBJECT INDEX	282
AUTHOR INDEX	286
ADDENDUM	288



Apparatus of DE SAUSSURE to test the effect of exposing the roots of young chestnut plants to different gases; the lower parts of the roots dipped into distilled water. Plants with roots exposed to carbon dioxide died in 7 or 8 days; those with roots exposed to nitrogen or hydrogen died in 13 or 14 days; those with roots exposed to common air were still flourishing after 21 days. (pp. 104-5, *Recherches chimiques sur la Végétation*.)

PREFACE

The central and most influential figure in the history of agricultural chemistry is JUSTUS VON LIEBIG. His unrivaled preeminence as a chemist for over a half a century brought world-wide attention to every contribution of his pen; it was therefore but natural when his book upon "Organic Chemistry in its Applications to Agriculture and Physiology" was published in 1840 and that it should have obtained immediately a most remarkable reception. It was translated into many languages, passed through numerous editions, and its message, widely circulated by a loyal band of LIEBIG's students, was brought to the attention of readers in every civilized country.

Unfortunately a number of errors have been passed down by some of LIEBIG's biographers and eulogists regarding his relationship to certain developments in agricultural chemistry during the important decade of the eighteen forties. It has been stated for example that LIEBIG was the first to demonstrate the errors of the humus theory, that he was the first to point out the necessity of mineral matter in the nutriment of plants, that he was the first to indicate the interrelationship of plant and animal life, and that he was the first to show that the heat of the animal body is a result of processes of combustion performed within the organism. Careful inquiry would have shown that these statements had been announced by previous investigators. It has been too often overlooked that in his "Organic Chemistry in its Applications to Agriculture and Physiology" LIEBIG was more a promulgator and defender of truths that had already been announced than a discoverer of new knowledge. The beginnings of agricultural chemistry can be traced back many centuries before the time of LIEBIG.

The purpose of the author in writing the present work has been to give a more accurate and complete account, than has hitherto appeared, of the origins of agricultural chemistry and of the relationships of LIEBIG's work to that of his predecessors. In doing this he has preferred so far as possible to let these predecessors in selected passages give their own accounts of the work selected for description, with no attempts at modernization of language. This volume is therefore primarily a source-book and while there can be a just difference of opinion in the choice of selective material, it is hoped that the various quotations and translations submitted will give the reader a good general perspective of developments in the history of agricultural chemistry from early beginnings down to the time of LIEBIG. Unless otherwise stated the various translations of original source material were made by the author.

In agricultural chemistry as in all other sciences the quest of truth is always accompanied by the commitment of errors. While a narration of errors should not be given undue prominence in a textbook of science, a detailed account of some of them must be given in a history of science, for mistaken theories, as in the case of phlogiston, have often been stepping stones to the discovery of truth. Moreover some doctrines, once rejected as false, were later found to contain a considerable amount of truth. The author has attempted in the present volume to give a balanced presentation of the stories of truth and error as they have developed side by side.

The decade following the publication of LIEBIG's "Organic Chemistry in its Applications to Agriculture and Physiology" is the most remarkable in the whole history of agricultural chemistry. In it occurred not only the publication of highly important works by BOUSSINGAULT, LAWES, LIEBIG, MULDER, WIEGMANN and others, but also the establishment of the modern artificial fertilizer industry, the founding of the Rothamsted Agricultural Experiment Station in England and the commencement of agricultural chemical research in the United States by HORSFORD, BECK, NORTON and others. This productive decade was the culmination of preceding centuries of agricultural chemical research and its termination, coinciding closely with the end of LIEBIG's work at Giessen, has been selected as a logical closing point for these chapters in the history of early agricultural chemistry. The history of developments since 1850 falls, therefore, outside the scope of the present volume. Readers who desire to follow the history of agricultural chemistry into this later more modern period are referred to the recent collaborative volume "Liebig and After Liebig," published by the American Association for the Advancement of Science, and to "Some References to the History of Agricultural Chemistry in the Century 1840-1940" contained in the Addendum at the end of this volume.

The date August 26, 1943, on which the closing paragraphs of this preface are being written coincides with the two hundredth anniversary of the birthday of ANTOINE LAVOISIER who established the basic principles on which the future development of experimental agricultural chemistry was to proceed. The year 1943, is also the bicentenary of the birth of THOMAS JEFFERSON, the friend of JOSEPH PRIESTLEY, who was not only a statesman and practical farmer but a close student of the developments in agricultural chemistry during his time. It is of interest to note that in the collection of JEFFERSON's scientific books at the Library of Congress there are works of HALES, DUHAMEL, HOME, WALLERIUS (MILLS' English translation), INGEN-HOUSZ, SCHEELE, LAVOISIER, and CHAPTAL—all European contemporaries of JEFFERSON and sketches of whose work are given in the present volume.

In conclusion the author desires to express his indebtedness and appreciation to Hon. HERBERT C. HOOVER and LOU HENRY HOOVER for permission to reproduce the woodcut of the lixiviation of wood-ashes from their translation of AGRICOLA's "De Re Metallica;" to Dr. LEONARD DOBBIN of the Alembic Club of the University of Edinburgh for permission to quote passages from his translations of the works of MAYOW and SCHEELE; to Miss EVA V. ARMSTRONG, Curator of the Edgar F. Smith Collection in the History of Chemistry, at the University of Pennsylvania, and to Mr. FREDERICK E. BRASCH, Chief of the Scientific Collection of the Library of Congress, for assistance in procuring photographic reproductions; to his wife Dr. LOUISE McD. BROWNE for her aid in preparing the index; and to Dr. FRANS VERDOORN, Editor of CHRONICA BOTANICA, for his many helpful suggestions in preparing this work for publication.

INTRODUCTION

Agricultural Chemistry Defined:—As the student delves into the history of the subject, he finds that there has long been a doubt both in America and Europe as to the legitimacy of the designation Agricultural Chemistry. There is certainly as much of physics and of biology in the operations of agriculture as there is of chemistry, yet the terms agricultural physics and agricultural biology are rarely employed, nor are the titles agricultural physicists and agricultural biologists applied to scientists upon the staffs of our agricultural colleges and experiment stations.

As far back as 1863 that delightful Connecticut essayist, "IK. MARVEL" (DONALD G. MITCHELL), discussed this subject very entertainingly in his "My Farm of Edgewood" (N. Y. 1864, pp. 223-4):—

"People talk of agricultural chemistry as if it were a special chemistry for the farmer's advantage. The truth is (and it was well set forth, I remember, in a lecture of Professor JOHNSON) there is no such thing as agricultural chemistry, and the term is not only a misnomer but it misleads egregiously. There is no more a chemistry of agriculture than there is a chemistry of horse-flesh or a conchology of egg-shells. Chemistry concerns all organic and inorganic matters; and if you have any of these about your barnyards, it concerns them; it tells you—if your observation and experience can't determine—what they are. Of course it may be an aid to agriculture; and so are wet weather, and a good hoe, and grub, and common sense and industry."

This criticism of the term agricultural chemistry, expressed so facetiously by "IK MARVEL", has been shared by many agricultural writers and to understand how this designation came into gradual use and then acquired such a variety of confused meanings we must go a long distance into past history. In its generally accepted sense, the term "agricultural chemistry" means the chemistry of farm operations whether performed by nature or conducted by man, and the discussion of the validity of the expression "agricultural chemistry" centers at once about the meaning of the word "agriculture".

The word agriculture is of ancient Roman origin and means literally "field-cultivation" but this restricted definition was amplified by the ancient writers to include any farm occupation practiced by a cultivator of the soil such as stock raising, dairying, forestry, fruit growing, bee-keeping and the like. The old Greek and Latin treatises upon agriculture discuss a large variety of subjects, such as weather; soils; manures; cultivation of crops; fruits and vegetables; the care of animals, poultry, bees and fish; and the utilization upon the farm of its produce for the manufacture of oil, wine, cheese, and other commodities. The same scope of subject matter was adhered to by the medieval writers upon agriculture, as CRESCIENTO, and it has been followed with few departures even down to modern times.

Eminent European teachers have discussed the complexity and validity of the term agricultural chemistry in the introductions to their lectures and books. Thus Professor BERNHARD TOLLENS at the commencement of his course on agricultural chemistry at Göttingen University defined the title of his lectures as a collective term:—

"Agricultural Chemistry is an applied science. It considers whatever has a relationship to agriculture in other sciences, more especially in chemistry, physics, geology,

botany and plant physiology, but more exactly than would be possible from the viewpoint of any single one of these sciences."

Professor ADOLF MAYER of Heidelberg in his well-known "Lehrbuch der Agrikulturchemie" discusses this mutual interrelationship of sciences in the first chapter of his book (4th ed. 1895, pp. 3-4) :—

"It is necessary in agricultural chemistry for the investigator to make use of very different scientific disciplines, whether they be physics, mineralogy, plant or animal physiology, without, however, abandoning the province of chemistry. The complex phenomena of agriculture permit no pedantic separation of the individual sciences that are mutually concerned therewith and whoever, in his experimental work, attempts to apply only a single one of these sciences to the problems that confront practical agriculture will in most cases completely fail The established term Agricultural Chemistry indicates that of the various other related sciences chemistry was the first to have a voice in considering the basic principles of agriculture. Strictly speaking we could speak just as well of Agricultural Physics or of Mineralogy or Plant Physiology in the service of agriculture. But following the precedent of others, as well as for the sake of simplicity, I prefer to call the sum total of all these different scientific approaches to husbandry Agricultural Chemistry."

The attitude of MAYER seems upon the whole to be sensible and correct. We have only to consider that nature does not confine its operations to any one of the physical sciences which man for the sake of convenience has marked off for his special study and consideration. Such demarcations are purely artificial where many sciences are involved. Agronomy, plant physiology, animal nutrition, and other so-called agricultural sciences all make use of chemistry. Agricultural chemistry draws in turn upon physics, mineralogy, geology and other fields of knowledge. It approaches the problems of agriculture chiefly but not exclusively from a chemical viewpoint.

In the late 1870s a reaction began in Germany to abolish the chairs of Agricultural Chemistry in some agricultural institutions and to distribute its fields of interest among the departments of pure chemistry, physics, plant physiology and the various practical branches of applied agriculture, such as agronomy, dairying, animal nutrition and crop utilization. The movement, however, was not a general success and the former courses in agricultural chemistry were in some cases reestablished. As MAYER (*loc. cit.*, p. 4) in his discussion of the subject has pointed out, the great modern developments in the theory and application of fertilizers, to cite a special case, could only have developed from the efforts of agricultural chemistry.

While there has been an occasional misapplication of the phrase "agricultural chemistry", it seems necessary to accept it as a conventional term of general use, just as such expressions as "medical chemistry" and "municipal chemistry" are employed to indicate special branches of applied science. We have already defined agricultural chemistry as the chemistry of farm operations. For a more specific interpretation of the term we may define agricultural chemistry as that branch of applied science which deals with the chemical composition and mutual chemical relations of soils, fertilizers, crops, and farm animals in so far as they concern the production upon the farm of agricultural supplies. The chemical rôle of the atmosphere and water in their relations to crop production must also be considered. The chemistry of the plant's contact with the three environmental agencies of

earth, water, and air is the central dominant fact of all agriculture. This has so far outweighed all other considerations that many writers upon agricultural chemistry have preferred to make it the sole object of their discussions. The mutual relationships of crops to animals and of animals to crops constitute, however, such an important part of agricultural science that they must be considered in any comprehensive treatise of agricultural chemistry.

The utilization upon the farm of agricultural raw materials for the production of butter, cheese, cider, wine, essential oils, sirup, honey, sugar, preserves, etc., is considered by some as a part of the legitimate field of agricultural chemistry and this may be allowed in so far as these pursuits form an integral part of the farm operations. But complications have arisen in extending this principle to the chemical control and chemical utilization of agricultural products after they have left the farm. Such applications belong more properly to the fields of regulatory and industrial chemistry. The examination of farm products for adulteration and their utilization for the manufacture of leather, paper, industrial alcohol, etc., are generally excluded from the accepted province of agricultural chemistry.

"The chymists, in their searches after truth, are not unlike the navigators of SOLOMON'S Tarshish fleet, who brought home from their long and tedious voyages, not only gold, and silver, and ivory, but apes and peacocks too; for so the writings of several (for I say not, all) of your hermetick philosophers present us, together with divers substantial and noble experiments, theories, which either like peacocks' feathers make a great shew, but are neither solid nor useful; or else like apes, if they have some appearance of being rational, are blemished with some absurdity or other, that when they are attentively considered, make them appear ridiculous."

—the Hon. ROBERT BOYLE

Chapter I

AGRICULTURAL CHEMISTRY IN ANCIENT TIMES

Theories:—Agricultural Chemistry is an experimental science and the use of carefully controlled experiments for the discovery of new knowledge is of comparatively recent origin. Certain agricultural chemical arts, such as composting, baking, dairying, fermenting, oil-making and food preservation were all well developed before men began to speculate as to the nature of the processes that underlie these operations. Crude mythological conceptions were first employed among the early Egyptian, Chaldean, Indian, and Chinese writers to explain the phenomena of agriculture and it was not until the time of the Greeks in the sixth century B. C. that philosophic ideas of a unifying character began to be introduced.

Early Greek Nature Philosophers (640-430 B. C.):—THALES OF MILETUS (about 640-546 B. C.) was the first Greek who sought to reduce the manifold operations of Nature to the operations of a single common principle which he believed to be water. "All things are water" (*πάντα ὕδωρ ἐστί*) was the sum and substance of his teaching. He was led to this conception, according to ARISTOTLE, by his observation of the part which moisture plays in the production and maintenance of plant and animal life. This first unifying conception had a great influence upon the subsequent history of agricultural chemistry, survivals of this belief persisting until after the commencement of the nineteenth century.

ANAXIMENES OF MILETUS, a younger contemporary of THALES, proposed air as the original element from which the universe was derived, while HERACLITUS OF EPHEBUS (540-475 B. C.) considered fire to be the primal substance of all material existence. Everything, according to HERACLITUS, was in a state of continued flux, or, as he expressed it, "all things flow" (*πάντα ῥεῖ*). Fire, by successive degrees of condensation through air and water, was finally changed to earth, while earth, by successive degrees of rarification through water and air, might be reconverted into fire. By these transformations of matter along the so-called downward (*κάθοδος*) and upward (*ἀνόδος*) ways, all cosmic phenomena were explained.

EMPEDOCLES OF AGRIGENTUM (about 495-435 B. C.), instead of regarding one principle as the basic constituent of matter, recognized four elements, earth, water, air and fire, as the roots from which all existence was derived. According to his conception, the multitude of material substances was due to a uniting of the four elements into different combinations which were regulated upon the one hand by a condition of love or attraction and upon the other by a state of hate or repulsion. The theory of four elements, proposed by EMPEDOCLES and adopted by PLATO and ARISTOTLE, became the governing doctrine in agricultural chemistry for the next two thousand years.

ANAXAGORAS OF CLAZOMENAE (about 500-430 B. C.), a contemporary of EMPEDOCLES, held that the constituents of rocks, plants, and animals have existed in the world since the beginning as infinitely small miniatures of the metals, wood, grain, milk, blood and countless other objects of nature.

These so-called seeds (*σπέρματα*) of things, infinite in kind and number, were scattered indistinguishably throughout the material mass of the universe and could only be segregated and combined with their own species to form the objects of sense perception by the action of an inherent infinite Mind (*νοῦς*). This conception of ANAXAGORAS was afterwards made by ARISTOTLE the basis of his doctrine of *homoioimeria* (*ὁμοιομερῆ*, i.e., like parts).

Democritus of Abdera (about 460–360 B. C.): — DEMOCRITUS was the Greek philosopher who exercised the greatest influence upon the developments of modern chemistry. Influenced perhaps by ANAXAGORAS but departing from his doctrine of miniatures, he conceived all matter to be composed of exceedingly small indivisible atoms, which differed in form, weight and size. The basic material of these indestructible and unchangeable atoms was the same; it was only the variation in their form, size and arrangement that caused the differences in the properties of substances. DEMOCRITUS regarded the spaces between the atoms as a void and explained the variations in density of substances by supposing the atoms to fill a given space with a greater or lesser degree of compactness. He held matter to be indestructible and denied the convertibility of one kind of atom into another. The changing forms of matter were attributed to the disintegration of older atomic combinations and to the reconstruction of newer arrangements.

The atomic theory of DEMOCRITUS was criticized by ARISTOTLE because of its purely mechanistic explanations and because the reciprocal convertibility of the four elements was denied. The evaporation of water was explained by the Aristotelian school as an actual transmutation of the liquid into air, whereas DEMOCRITUS and the atomic philosophers attributed the phenomenon to the separation of the invisible atoms of water by wider intervals of space. When these spaces were reduced and the atoms came closer together the liquid state of water was restored. We know now that the explanation of DEMOCRITUS, with its recognition of different states of the same substance, was much nearer the truth.

One of the best accounts of the atomic theory of DEMOCRITUS, as interpreted by his follower EPICURUS (347–270 B. C.), is contained in the Latin poem of LUCRETIIUS (about 98–55 B. C.) on the "Nature of Things" (*De Rerum Natura*), from the second book of which the following abstract has been made: —

Although objects may be motionless, the atoms which compose them are in constant movement, but these movements cannot be seen because they are far beyond the range of vision. The atoms are of different sizes and shapes. The finest atoms, as those of light, can pass through a translucent substance, as horn, which the larger atoms of water cannot penetrate. For the same reason wine flows quickly and oil sluggishly through a strainer. Substances of a pleasant taste, as honey and milk, have smooth round atoms while bitter substances, as wormwood, have jagged atoms which lacerate the tongue. Other substances of a spicy flavor, as the tartar of wine and elecampane, have atoms with slender projections that simply tickle the tongue. Very hard substances, as stones and metals, have atoms with hooks which hold them in close combination. Liquid substances have smooth round atoms which do not permit them to cohere. Sea-water, in addition to its round atoms, contains dissolved atoms of salt with jagged projections which give it a bitter taste. If sea-water be filtered through earth the salt is held back by the retention of its rougher and more easily captured

particles while the water which flows through, having only round and more passable particles, is sweet.

The number of atoms is infinite but the number of their shapes is finite. The more properties an object possesses, the greater is the variety of its elementary atoms. The earth for example must have a great variety of elements for out of it are produced not only the immense abundance of crops and pastures, but also trees, animals and men.

Sheep, horses and cattle though feeding on grass from the same field and drinking from the same stream, yet preserve throughout life the distinctive forms and appearance of their kind, so great is the diversity of elements in each kind of grass and stream. The bones, blood, veins, viscera, sinews and all the other organs of each animal differ from one another and are composed of different atoms of unlike shape. Combustible materials also contain elementary particles which are dispersed on burning into fire and ash. Many other things differing in color, taste and smell are composed of numerous elements of varying atomic shapes, just as the same letters of the alphabet enter into the structure of different words and sentences. The words and sentences vary but the letters are the same. The elements, however, do not unite at random but by a fixed law for when mixed food is eaten the appropriate particles pass to their places in the frame of the body while those which are unsuitable are eliminated.

Animals are begotten from senseless elements, just as living worms are seen to issue forth from putrid dung. Other things change in the same way — grass, foliage and water into cattle and the flesh of cattle into our own bodies. Stones, wood and earth, however mixed together, are unable to produce life; this can only be produced by definite rearrangements of certain of their atoms.

Mother earth when fructified by rain gives birth to crops for the nourishment of man and beast. But that which came from earth must return to earth and that which came from air to air. Death, however, does not destroy matter but only breaks up the union of its elements which are then recombined into other forms.

Space is unlimited, the stars are countless and the atoms of matter infinite so it is reasonable to suppose that there are other worlds similar to this populated with animals and men. The world itself, however, must finally share the fate of its creatures and will eventually pass away.

The atomic philosophy of DEMOCRITUS, with its account of the continual circulation of indestructible and non-convertible elementary atoms through soils, plants and animals, is the earliest expression of a comprehensive scientific theory of agricultural chemistry. It represents the first praiseworthy attempt to explain evaporation, adsorption, viscosity, diffusion, solidity, density, nutrition and numerous other phenomena that are discussed in modern text books of chemistry and physics. In the system of DEMOCRITUS are found also many intriguing false conceptions, such as that of spontaneous generation, which have been perpetuated, like the hypothesis of THALES, with recurring persistence even down to modern times. But taken all in all the atomic conception of DEMOCRITUS is one of the greatest achievements of the human mind and had it met with immediate acceptance the rise of modern chemistry might have been advanced two thousand years. We may indeed date the commencement of modern chemistry from the seventeenth century when under the influence of BACON, BOYLE, NEWTON and other leaders the atomic conception of DEMOCRITUS was revived and the physical theories of ARISTOTLE overthrown.

Aristotle (384–322 B. C.):—The opposing system of ARISTOTLE, with its insistence upon the mutual convertibility of the four elements, won the ascendancy in ancient and medieval times over the atomic conception of DEMOCRITUS. The doctrine of elementary transmutation had its pernicious effects not only in encouraging the pretensions of alchemy but in hinder-

ing the efforts of the eighteenth and nineteenth centuries to lay the foundations of a true science of agricultural chemistry.

The mistake should not be made, however, of underestimating the great genius and influence of ARISTOTLE who was the first philosopher to systematize science, to write encyclopedic treatises of its different branches and to formulate the rules of inductive reasoning by which the method of scientific discovery should proceed. He pointed out that the first step in every investigation is to collect a sufficient number of facts by observation of natural phenomena, before attempting to explain underlying laws and principles. His inability to form correct explanations, was not due to the fault of the method but to his reliance on incorrect observations and to his use of faulty analogies and to *a priori* methods of reasoning by which observations were explained on the basis of preconceived ideas. Of experimental methods of investigating natural phenomena he had only the faintest conception.

ARISTOTLE's opinions regarding the composition of mineral matter, plants and animals are found widely scattered in his various works on "Physics", "Meteorology", "The Heavens", "Generation and Decay", "Respiration", "The Soul", "History of Animals", "Parts of Animals", and "Generation of Animals". The works on "The Universe", "Plants", "Colors", and "The Problems", although probably not written by ARISTOTLE himself but by members of his school, contain much information of historic interest.

ARISTOTLE held that the material constituents of the world were formed from mixtures of the four elements whose motions were upward with the lighter elements, fire and air, and downward with the heavier elements, water and earth. To these four elements he added a fifth hypothetical element — the circumambient ether, which he employed to explain celestial phenomena and whose motion, high above the other elements, he considered to be circular. Upon his conception of four terrestrial elements, ARISTOTLE superimposed a doctrine of qualities, or forces. Fire, the lightest element, was regarded as hot and dry; air, the next highest, as hot and wet; water being more heavy, as wet and cold; and earth, the heaviest, as cold and dry.

The doctrine of qualities was much used by later agricultural-chemical writers to explain certain properties and interrelationships of soils and of plant and animal life. The hypothesis had certain attractions in that it seemed to explain how the elements combined. For the actual union of two opposites, Greek philosophic ideas required the action of an intermediary which shared some of the qualities of the two elements or substances. Fire and water, for example, having no qualities in common, cannot unite directly. These opposites, however, can be made to combine by the intermediation of air, which shares the warmth of fire and the wetness of water, or by the interaction of earth, which shares the dryness of fire and the coldness of water. By means of other similar combinations, in greatly varying proportions, were formed the immense multitude of substances that compose the mineral, vegetable and animal kingdoms of nature. A distinction was made, however, by ARISTOTLE between different kinds of combinations. He recognized synthesis (*σύνθεσις*, i.e., putting together), or mechanical mixture, in which the individual particles maintain their identity; *mixis* (*μίξις*), or union, in which the identity of the combining particles is lost;

and crasis (κράσις), or blend usually applied to the mingling of liquids as wine and water. ARISTOTLE's mixis comes nearest to the idea of chemical combination, although with the difference that a mixis of two substances like the fusing together of two metals, could take place in all proportions.

By the union, or mixis, of the four elements in the soil, ARISTOTLE supposed the nutritive organic matter of plants to be generated in the form of exceedingly minute particles, or homoiomeria, which being assimilated through the roots were deposited unchanged in the tissues and organs of similar homoiomeric character. According to this conception, which was taken from ANAXAGORAS, the plant possessed no respiratory, metabolic,

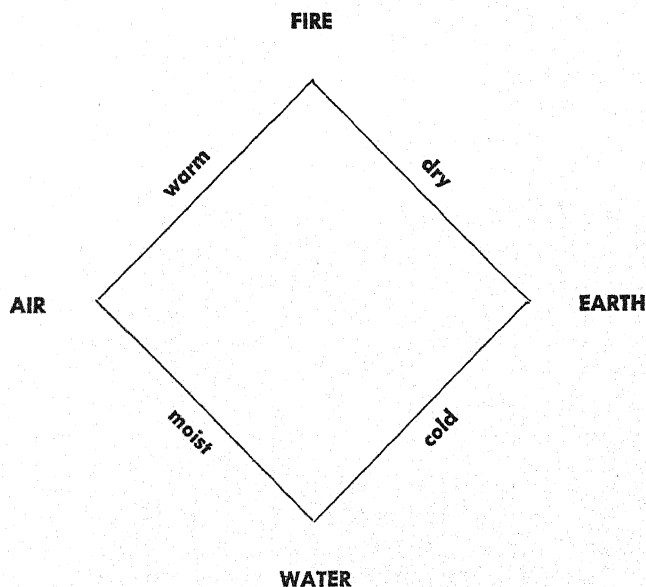


FIG. 1. — *Diagram of the four elements and qualities according to Aristotle.* — Fire which is warm and dry is opposite Water which is cold and moist. Earth which is dry and cold is opposite Air which is moist and warm. Each element shares one property with the adjacent element.

or excretory functions. In the same way the bones, blood, milk, hair and other parts of animals were supposed to come from preformed infinitely small miniatures of these bodily constituents in the grass and other vegetable products which they had eaten. ARISTOTLE's doctrine that plants derived nourishment through their roots from preformed organic matter in the soil held sway for over two thousands years and found its final development in the humus theory of plant nutrition which prevailed in the eighteenth and nineteenth centuries until it received its final overthrow at the hands of LIEBIG in 1840.

Experimental Science in the later Greek Epoch: — The weakness of all the ancient systems of natural philosophy was their speculative character and their failure to establish their doctrines upon the basis of experimental proofs. In the rare instances where empirical demonstrations were

attempted, experiments were conducted not for the purpose of discovering new knowledge but to vindicate traditional doctrines.

This is well illustrated by the case of PHILO OF BYZANTIUM (Second Century B. C.) who was the first to describe the familiar experiment of burning a candle under an inverted vessel over water (SCHMIDT 1899, pp. 476-8). According to PHILO the flame of the candle converts some of the corpuscles of air into the finer particles of fire which escape through the pores of the glass vessel, as is evident by the warmth imparted to the hand. The partial vacuum, thus created, causes the water to ascend into the neck of the vessel. This very ingenious but incorrect explanation satisfied the minds of men for many centuries thereafter.

Heron of Alexandria.— Experimental science in ancient times attained its highest development in Alexandria. This commercial city was also a great centre of Greek culture and its famous library attracted scholars from all parts of the Mediterranean world. Science was studied there in both theoretical and practical relations. The technicians of Alexandria were skilled in constructing elaborate apparatus of metal and glass, as we know from reading the "Pneumatics" and other works of the Greek geometer and mechanician, HERON, whose date, according to the best estimates, was in the first, or second century A. D. HERON describes in his works not only the construction of ingenious automatic devices operated by compressed air, steam, etc., but he gives also explanations of the principles that underlie their operation. His discussions are interesting illustrations of how the theory of the mutual transmutability of the four elements was applied experimentally.

Some five centuries before HERON's time, EMPEDOCLES described an experiment with a clepsydra which proved air to be a material body. This was demonstrated in a more complete way by HERON in his discussions of vacua and of the corpuscular nature of air. The following passage is translated from the introduction to his "Pneumatics":—

"Vessels that seem to be empty to most people are not empty, as they suppose, but are full of air. But, air, as practical physicists agree, is composed of fine, minute, entirely invisible corpuscles. If now one should pour water into an apparently empty vessel, the volume of air that will come out is the same as the volume of water that is poured in. The truth of this any one can see from the following experiment. If one inverts an apparently empty vessel and plunges it vertically into water the latter will not flow in, even if the vessel is completely submerged. Hence it is plain that the air is a body and therefore prevents the entrance of water, because of its filling the entire inner space of the vessel. If now a hole should be bored in the bottom of the vessel water will flow into it through the mouth below while the air escapes through the hole above. Again if before boring the hole in the bottom of the vessel, you should lift the latter vertically from the water and reverse it, you will see its inner surface to be just as dry as before submergence. It must therefore be taken for granted that the air is a body.

"Wind is nothing more than air in motion. This is shown if you hold your hand over the hole in the bottom of the vessel while the water flows in below, when you can feel the wind, which is nothing more than the air in the vessel being forced out by the water. The supposition, therefore, that there is in objects something in the nature of a vacuum continuous of itself is not sustained, but rather the view that it is distributed in small parts in the air, water and other bodies. If the diamond should seem to be an exception to this nature of a vacuum, because fire cannot penetrate it and because when struck on an anvil by a hammer it is not broken but pierces both anvil and hammer, this is due to its extraordinary compactness, for the corpuscles of

fire being thicker than the vacua of the stone cannot penetrate them but only touch its outer surface. Therefore since the corpuscles of fire do not penetrate it as they do other bodies the diamond is not heated.

"The corpuscles of the air collide with one another, but without union of a single particle, for there are vacant spaces between them just as with the sand of the sea shore. For just as the particles of sand are separated by spaces of air, so are the air corpuscles separated by intervening vacua. If now an outer force be applied it will compress the air and cause it to contract into the spaces of its vacua, as a result

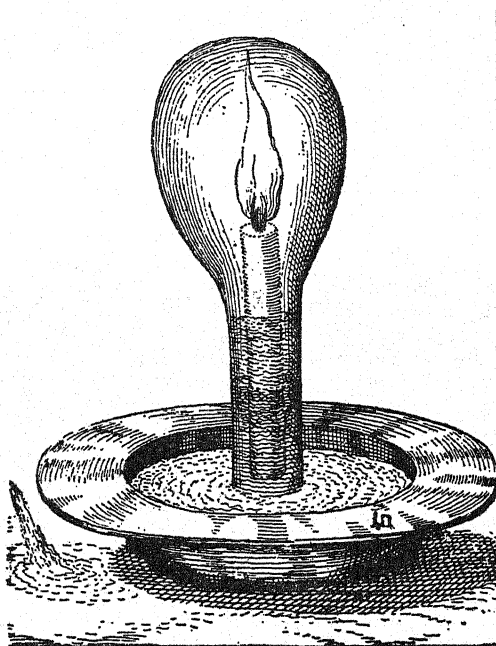


FIG. 2. — *The Candle Experiment of Philo of Byzantium (150 B.C.).* — A burning candle in a basin of water is covered with an inverted flask. The candle finally goes out and water rises into the neck of the flask. PHILO held that the flame of the candle transformed some of the corpuscles of air into the finer corpuscles of fire which escaping through the pores of the glass left a partial vacuum behind. The true explanation was not found until the 18th century A.D., after the discoveries of hydrogen and oxygen. Illustration taken from ROBERT FLUDD's "Technica Macrocosmi Historia" (1618), p. 471.

of its corpuscles being forced together. If the pressure is released the air is restored again to its former condition in consequence of the tension of its corpuscles in exactly the same way that scrapings of horns and dry sponges return after compression to their original space and bulk. For corpuscles move quickly in a vacuum, nothing impeding or resisting their passage until they collide with one another.

"If now one should take a very light vessel with narrow orifice, place it to his mouth, suck out the air and then let go, the vessel will remain hanging to his lips, for the vacuum draws the flesh in so as to fill the emptied space. From this it is clear that a continuous empty space exists within the vessel. This is evident also from another fact. Whenever men wish to fill the so-called medical eggs, which are of glass and have a narrow neck, with a liquid, they suck out with the mouth the air that is in them and then covering the orifice with the finger invert it into the liquid. The finger

being removed the water is drawn up into the evacuated space, although the movement of a liquid upward seems contrary to nature" (SCHMIDT 1899, pp. 4-10).

In his discussion of the corpuscular nature of air HERON anticipates quite accurately some modern conceptions regarding the behaviour of gaseous molecules under varying pressures. The term *ἐνθρόια*, or tension, to designate the resiliency of compressed air, is the equivalent of the expression "spring of the air" used by BOYLE in the seventeenth century.

HERON proceeds next to discuss some effects of the supposed transmutation of air corpuscles by fire. The conception adopted by PHILO OF BYZANTIUM to explain the rise of water in his candle experiment is employed by HERON to explain the partial vacuum that is produced in a heated cupping glass, in which connection the transmutation of other elements than air is also considered.

"When cupping-glasses are placed against the body not only do they not fall off, although somewhat heavy, but they draw up also the adjacent matter through the pores of the body for the following reason: The fire that heated the cupping-glass decomposes and rarefies the air that is in it, just as other bodies are consumed by fire which transforms them into finer elementary particles, namely water, air and earth. That they are actually consumed is evident from the carbonaceous residue, which, although occupying the same or a little less space than before combustion, nevertheless differs greatly with respect to the weight which the material had at the beginning. The parts of the bodies that were consumed pass off in smoke as a fiery, aerial or earthy substance. The lightest parts of what is consumed rise to the highest region where fire belongs; the parts that are somewhat denser than these pass into the region of air, while those that are still coarser, although borne along with the others for a time by the continuous draft, fall again downward and unite with the earthy materials. Water also changes into air when decomposed by fire. For the vapors that rise from boiling kettles are nothing else than the attenuated particles of the liquid changing into air. That fire decomposes and transforms substances that are denser than itself is therefore evident.

"Also as a result of the exhalations of the earth denser substances are transformed into finer ones. For dews are produced only when the water in the earth is rarefied by the evaporation, which is caused by a fiery emanation when the sun is under the earth and heats the place on that side. If the latter is of a sulphurous or asphaltic nature it intensifies the exhalation on being warmed. The hot springs that are found in the earth are explained by a similar cause. The lighter particles of the dew change into air, but the heavier ones, although borne along for a time by the force of the exhalation, fall back to earth again as a result of the cooling that comes after sunset. Winds also are the result of a strong exhalation; the air is thereby expelled and rarefied and it sets in continuous motion what is next to it. The movement of the air, however, is not uniformly rapid in every place, but is stronger at the point of exhalation and weaker when more remote from this centre of movement, just as happens when heavy objects are thrown upwards. For the latter move quicker in the lower region near the place of the projecting force, but slower higher up. When this projecting force is no longer active then the objects return again to their natural place, which is down below. If the projecting force carried them forward with equal speed, they would never stop, but now, the force gradually slackening and spending itself, the speed of projection comes to an end.

"Water also is transformed into earthy substance for whenever we pour water into a hollow place in the ground, it disappears after a short time and is absorbed by the earthy substance, uniting with it and becoming itself earth. If any one should say that it is neither transformed nor absorbed by the earth but is evaporated after absorption by the heat of the sun or of some other body, it can be shown that he reasons falsely, for the same amount of water when placed in a vessel of glass, bronze, or other dense material and exposed to the sun for a long time, undergoes only a small diminution in quantity. So that the water is transformed into the substance of the soil. Mud and slime are transformation products of water into earth.

"Finer substance is transformed into the more dense, just as occurs with the flame of lamps that become extinguished from lack of oil. The flame shoots upward for a time, as if striving to reach its proper place, which is the highest region above the atmosphere, but overcome by the excess of air between, it can no longer reach its abode and mixed with and bombarded by the corpuscles of air becomes air itself. A similar conversion must be supposed to take place with air when it is enclosed in a small vessel and plunged with this into water. As soon as the vessel is opened with the mouth uppermost water rushes in but the air that tries to escape is overcome by the excess of water, and is mixed and dashed about until it becomes water. In

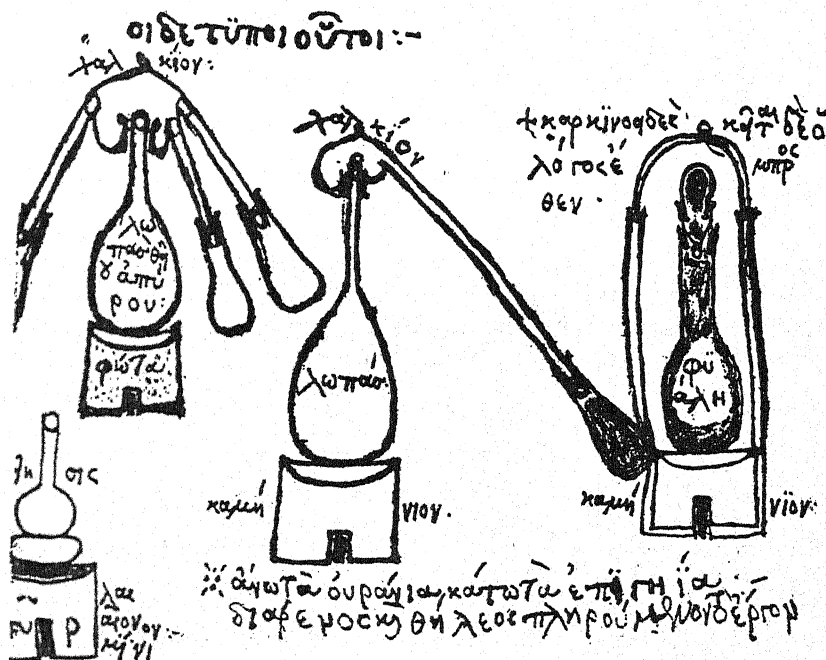


FIG. 3. — Sketches of Laboratory Apparatus of the late Greek Period. — Four furnaces with sand-baths support two alembics (with single and triple condensing tubes and recipients) and two types of digestion flasks. The apparatus of this period begins to assume a modern aspect. From a Greek manuscript of the 15th century in the *Bibliothèque nationale* of Paris.

the same way the air in the cupping glass is decomposed and attenuated by fire and escaping through the pores of the vessel leaves a vacuum within that draws up adjacent matter of whatsoever kind it be" (*loc. cit.*, pp. 10-16).

HERON's remarks about the weight of substances before and after combustion is an illustration of how the Greek experimenters approached at times a discovery and then went astray from a failure to see the import of their observations. Without knowing it HERON had at his command every device and material necessary for establishing the composition of the combustion products of plant and animal substances. He was prevented from forming a correct explanation of his experimental observations by adhering

to a false system of scientific inquiry which, working by the unproductive *a priori* method, employed experiments to demonstrate a preconceived hypothesis and not to discover new truth. Had HERON only followed up his observation by investigating the amounts of ash and the nature of the evolved gaseous products in the materials which he ignited he might have initiated a vast new field of scientific inquiry. The problem of combustion, however, had to wait until the time of LAVOISIER before its final solution.

No advancement beyond the chemical theories expressed by HERON was made during the next 1200 years. The old Greek conceptions of the four elements and of the transmutation of water into earth continued to hamper the progress of agricultural science until after the beginning of the nineteenth century.

Practices: — The ancient Greek and Roman writers upon agriculture compiled the results of long ages of practical experience. Their observations upon the best choice of soils, the benefits of different organic and mineral manures, the enrichment of land by cultivation of leguminous crops, and the advantages of fallowing, mulching, crop-rotation and other practices formed the basis of a system of husbandry that in many particulars was recognized as correct even down to the present day. Many hypotheses, of a speculative, astrological, mystical, or superstitious character, were advanced in the course of the centuries as reasons for some of these practices, but the true scientific explanations could not be found until after the beginning of modern science.

Caius Plinius Secundus (23-79 A. D.): — PLINY, called "the Elder" to distinguish him from his nephew PLINY "the Younger", in the intervals of his official duties in various parts of the Roman Empire, compiled the results of his extensive observations and readings in an encyclopedic work of 37 books, entitled "Historia Naturalis" which was completed only two years before PLINY's death during the eruption of Vesuvius in 79 A. D. Since PLINY's Natural History gives one of the best accounts of agricultural practices in Greco-Roman times the following references to Soils, Fertilizers, Agricultural Technology and Agricultural Analysis are taken from BOSTOCK and RILEY's six volume translation of this work.

Soils. — The ancient agricultural writers all recognized the fundamental importance of good soils not only for securing the best yield of crops but also for obtaining products of the highest quality. PLINY, whose travels to different parts of the Roman Empire gave him exceptional opportunities for wide agricultural observation, concluded that the chief factor in the production of high quality wines was land and soil, for the same variety of grape when transplanted to different regions produced wines of greatly varying character. The ancients had certain criteria for estimating the value of soils, such as color, texture, type of native vegetation, etc., but such observational facts were not sufficient to enable PLINY to cope with the difficult problems of land valuation. He described certain of these difficulties at some length in the following significant passage (Book 17, Chap. 3): —

"It is but rarely that the same soil is found suited to trees as well as corn: indeed, the black earth which prevails in Campania is not everywhere found suited

to the vine, nor yet that which emits light exhalations, or the red soil that has been so highly praised by many. The cretaceous earth that is found in the territory of Alba Pompeia, and an argillaceous soil, are preferred to all others for the vine, although, too, they are remarkably rich, a quality that is generally looked upon as not suited to that plant. On the other hand, again, the white sand of the district of Ticinum, the black sand of many other places, and the red sand as well, even though mixed with a rich earth, will prove unproductive.

"The very signs, also, from which we form our judgment are often very deceptive; a soil that is adorned with tall and graceful trees is not always a favourable one, except, of course, for those trees. What tree, in fact, is there that is taller than the fir? and yet what other plant could possibly exist in the same spot? Nor ought we always to look upon verdant pastures as so many proofs of richness of soil; for what is there that enjoys a greater renown than the pastures of Germany? and yet they consist of nothing but a very thin layer of turf, with sand immediately beneath. Nor yet is the soil which produces herbage of large growth always to be looked upon as humid; no, by Hercules! no more than a soil is to be looked upon as unctuous and rich, which adheres to the fingers — a thing that is proved in the case of the argillaceous earths. The earth when thrown back into the hole from which it has just been dug will never fill it, so that it is quite impossible by that method to form any opinion as to its density or thinness. It is the fact, too, that every soil, without exception, will cover iron with rust. Nor yet can we determine the heaviness or lightness of soils in relation to any fixed and ascertained weight: for what are we to understand as the standard weight of earth? A soil, too, that is formed from alluvion of rivers is not always to be recommended, for there are some crops that decay all the sooner in a watery soil; indeed, those soils even of this description which are highly esteemed, are never found to be long good for any kind of vegetation but the willow.

"Among other proofs of the goodness of soil, is the comparative thickness of the stem in corn. In Laborium, a famous champaign country of Campania, the stalk is of such remarkable thickness, that it may be used even to supply the place of wood: and yet this very soil, from the difficulty that is everywhere experienced in cultivating it, and the labour required in working it, may be almost said to give the husbandman more trouble by its good qualities than it could possibly have done by reason of any defects. The soil, too, that is generally known as charcoal earth, appears susceptible of being improved by being planted with a poor meagre vine: and tufa, which is naturally rough and friable, we find recommended by some authors. VIRGIL, too, does not condemn for the vine a soil which produces fern: while a salted earth is thought to be much better entrusted with the growth of vegetation than any other, from the fact of its being comparatively safe from noxious insects breeding there. Declivities, too, are far from unproductive, if a person only knows how to dig them properly; and it is not all champaign spots that are less accessible to the sun and wind than is necessary for their benefit. We have already alluded to the fact, that there are certain vines which find nutriment in hoar frosts and fogs.

"In every subject there are certain deep and recondite secrets, which it is left to the intelligence of each to penetrate. Do we not, for instance, find it the fact, that soils which have long offered opportunities for a sound judgment being formed on their qualities have become totally altered? In the vicinity of Larissa, in Thessaly, a lake was drained; and the consequence was, that the district became much colder, and the olive-trees which had formerly borne fruit now ceased to bear. When a channel was cut for the Hebrus, near the town of Aenos, the place was sensible of its nearer approach, in finding its vines frost-bitten, a thing that had never happened before; in the vicinity, too, of Philippi, the country having been drained for cultivation, the nature of the climate became entirely altered. In the territory of Syracuse a husbandman, who was a stranger to the place, cleared the soil of all the stones, and the consequence was, that he lost his crops from the accumulation of mud; so that at last he was obliged to carry the stones back again. In Syria again, the ploughshare which they use is narrow, and the furrows are but very superficial, there being a rock beneath the soil that in summer scorches up the seeds.

"Then, too, the effects of excessive cold and heat in various places are similar; thus, for instance, Thrace is fruitful in corn, by reason of the cold, while Africa and Egypt are so in consequence of the heat that prevails there. At Chalcia, an island belonging to the Rhodians, there is a certain place which is so remarkably fertile, that

after reaping the barley that has been sown at the ordinary time, and gathering it in, they immediately sow a fresh crop, and reap it at the same time as the other corn. A gravelly soil is found best suited for the olive in the district of Venafrum, while one of extreme richness is required for it in Baetica. The wines of Pucinum are ripened upon a rock, and the vines of Caecubum are moistened by the waters of the Pomptine marshes; so great are the differences that have been detected by human experience in the various soils. CAESAR VOPISCUS, when pleading a cause before the Censors, said that the fields of Rosia are the very marrow of Italy, and that a stake, left in the ground there one day, would be found covered by the grass the next: the soil, however, is only esteemed there for the purposes of pasturage. Still, however, Nature has willed that we should not remain uninstructed, and has made full admission as to existing defects in soil, even in cases where she has failed to give us equal information as to its good qualities: we shall begin, therefore, by speaking of the defects that are found in various soils.

"If it is the wish of a person to test whether a soil is bitter, or whether it is thin and meagre, the fact may be easily ascertained from the presence of black and under-grown herbs. If again, the herbage shoots up dry and stunted, it shows that the soil is cold, and if sad and languid, that it is moist and slimy. The eye, too, is able to judge whether it is a red earth or whether it is argillaceous, both of them extremely difficult to work, and apt to load the harrow or ploughshare with enormous clods; though at the same time it should be borne in mind that the soil which entails the greatest amount of labour is not always productive of the smallest amount of profit. So, too, on the other hand, the eye can distinguish a soil that is mixed with ashes or with white sand, while earth that is sterile and dense may be easily detected by its peculiar hardness, at even a single stroke of the mattock" (*loc. cit.*, Vol. 3, pp. 446-50).

"For the culture of the cereals, too, the same land is generally looked upon as the more improved the oftener it has been allowed to rest from cultivation, a thing that is not the case with vineyards; for which reason all the greater care is required in the selection of their site, if we would not have the opinions of those to appear well founded who entertain the notion that the soil of Italy is already worn out. In other kinds of soil the work of cultivation depends entirely upon the weather; as, for instance, in those which cannot be ploughed just after rain, because the natural exuberance of the earth renders it viscous and cloggy. On the other hand, in Byzacium, a district of Africa, and a champaign country of such singular fertility as to render grain one hundred and fifty fold, the soil is such, that in time of drought, not even bulls are able to plough it; while, on another occasion, just after a shower of rain, one poor ass, with an old woman to guide it, is quite sufficient, as ourselves we have witnessed, to do the ploughing. But as to amending one soil by the agency of another, as some persons recommend, by throwing rich earth over one that is poor and thin, or by laying a soaking light soil over one that is humid and unctuous, it is a labour of perfect madness. What can a man possibly hope for who cultivates such a soil as this" (*loc. cit.*, Vol. 3, p. 452)?

This passage, so illustrative of PLINY's industry in collecting information and also of his credulity and inability to sift evidence, is an honest confession of the limitations of soil science as it existed in ancient times. The agricultural chemist of today, with all his command of the aids of modern science and of those standards of exact measurement, of which PLINY deplored the lack, can read his statements with sympathetic interest, for he is still confronted with similar agronomic problems.

Fertilizers. — The value of animal manure for improving the productivity of the land was recognized as far back as the dawn of history. The respective merits of the dung of birds and poultry and of the excreta of horses, cows, goats, sheep, and men for different soils and crops were fully discussed by the agricultural writers of Greco-Roman times. The benefits of composts prepared from dung, vines, straw, stalks, leaves, weeds and other trash were likewise emphasized. Green manuring was also commended, as in the following passage from PLINY (Book 17, Chap. 6): —

"It is universally agreed by all writers that there is nothing more beneficial than to turn up a crop of lupines, before they have podded, with either the plough or the fork, or else to cut them and bury them in heaps at the roots of trees and vines. It is thought, also, that in places where no cattle are kept, it is advantageous to manure the earth with stubble or even fern" (*loc. cit.*, Vol. 3, p. 458).

Mineral manures were also employed for certain crops. PLINY writes again:—

"In more recent times it has been found that the olive thrives more particularly in soil that has been manured with the ashes of the lime-kiln."

PLINY mentions also (Book 19, Chap. 41) that nitre (the ancient natron or sodium carbonate) was used for hastening the maturity of cabbage. Marl, however, was the mineral fertilizer that was most discussed by PLINY, who states that it was chiefly employed for enriching the soil in the Gallic provinces and the British islands. He enumerates the white, red, columbine, argillaceous, tufaceous and sandy marls and describes the value of each kind for different lands and crops (pastures, cereals, hay, etc.) (Book 17, Chap. 4):—

"Every marl requires to be laid on the land immediately after ploughing, in order that the soil may at once imbibe its properties; while at the same time, it requires a little manure as well, as it is apt at first to be of too acrid a nature, at least where it is not pasture land that it is laid upon; in addition to which by its very freshness it may possibly injure the soil, whatever the nature of it may be; so much so, indeed, that the land is never fertile the first year after it has been employed. It is a matter of consideration also for what kind of soil the marl is required; if the soil is moist, a dry marl is best suited for it; if dry, a rich unctuous marl. If, on the other hand, the land is of a medium quality, chalk or columbine marl is the best suited for it" (*loc. cit.*, Vol. 3, p. 455).

PLINY states that some marls, when once applied to the land, would fertilize it for fifty years, whether for grain or hay, and in case of chalk, which was chiefly used in Britain, the good effects were found to last as long as eighty years. He mentions also that applications of limestone had been found to be particularly beneficial to the olive and vine.

The addition of soil from a fertile field in order to correct the sterility of barren lands, which was condemned by PLINY as a piece of madness, was an ancient practice that found a later basis of scientific support with the discovery in modern times of the benefits of soil inoculation. It is another illustration of how practice may antedate theory by thousands of years.

Agricultural Technology:— Ancient agriculture was to a high degree self-sufficient and the grain, olives, grapes, grass, milk, wool, etc., of each farm were utilized on their place of origin for the production of flour, bread, oil, wine, hay, cheese, cloth and other domestic products. There was thus established a large number of small agricultural industries, more or less of a chemical nature, whose varied activities formed an integral part of the farm operations. The equipment and technique of some of these rural processes merit a brief description.

Flour and Bread.— In making flour the grain was sometimes parched and then reduced with a pestle to flour which was freed from husks and

bran by bolting through sieves of horse hair. Another process consisted in cooking the grain to remove the husks and then, after drying in the sun, pounding and bolting as before. For large households the farmer had a stone mill, rotated by horses or slaves, for grinding the grain. In making bread the sifted flour was mixed with water or milk, a little salt was added, and the kneaded dough moulded into loaves or cakes which were then baked upon a hot hearth or in an oven of stone or baked clay. A little leaven was usually added to the dough. This was prepared by kneading fine wheat bran, or the flour of millet, barley, spelt, etc., with water, to which a little grape juice was sometimes added, allowing the mixture to ferment and then drying it in the sun. In most cases a little of the sour dough from a previous baking was used as leaven.

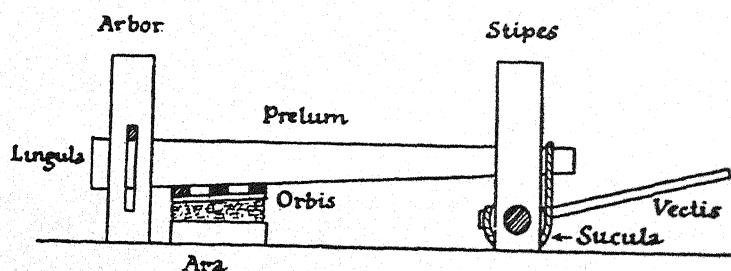


FIG. 4. — *Pliny's Beam and Drum Press with Latin names of parts.* — The *Lingula* was the fulcrum end of the beam (*prelum*) which was held between upright posts (*arbores*). The pulp of grapes, olives, etc., to be pressed was placed between the press-plate (*orbis*) and bed-support (*ara*). The movable end of the beam was drawn down by a rope wound about a drum (*sacula*) that was turned by a hand-spike (*vectis*). The upright posts that carry the drum were called *stipetes*. (DRACHMANN's "Ancient Oil Mills and Presses," p. 145).

Oil. — The stone edge-runner and beam press, which are still generally used in Mediterranean countries for crushing olives and expressing the oil, have a history that extends back over two thousand years into the period of Greek and Roman civilization. Classic descriptions of the ancient oil mills and presses are found in the works of CATO (234-149 B. C.), COLUMELLA (1st Century A. D.), PLINY, and other writers (DRACHMANN 1932). The olives, after being washed and dried, were crushed under the revolving stones of a trapetum, or edge-runner, and the oil was squeezed out from the pulp under a heavy beam press. Heating of the presses was thought to increase the extraction. The oil was filtered through osier baskets, heated in cauldrons and then poured into vats or jars to permit sedimentation of impurities. PLINY warns against loss of oil from deterioration if the olives are not pressed immediately. The ancients prepared oils also from the castor bean and other seeds. A few essential oils were made from plant materials by extraction with presses.

Fermented Beverages. — The manufacture of wine is one of the oldest agricultural arts. The process, as usually conducted in ancient times, consisted in tramping grapes with the bare feet to a pulp which was squeezed

under a beam or screw press. The expressed juice was then allowed to ferment and after a period of about nine days drawn off into jars which were sealed and stored until the matured wine was ready for consumption. In case of the best wines the aging process required several years and various expedients, such as exposure of the jars to the sun and to the smoke of burning wood in lofts, and treatment of the wine with powdered marble, gypsum, rosin, etc., were employed to hasten the process. According to PLINY, stored wine improved in quality up to the twentieth year, after which deterioration began. For making a stronger wine the grapes were sometimes allowed to dry partially before pressing and fermenting. A second quality wine was occasionally made by wetting the residual marc of the first pressing with water and repressing. Wine was also made from honey and the juices of apples, pears, pomegranates, medlars, mulberries, and other fruits.

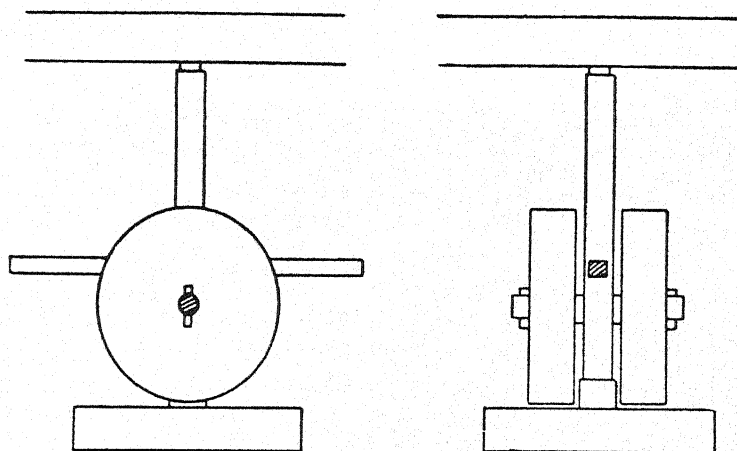


FIG. 5.—*The Oil-Mill of Columella (about 50 A.D.) as reconstructed by Drachmann (Ancient Oil Mills and Presses, p. 143).*—The axis of the two revolving mill stones passed through a vertical shaft which could be rotated on pivots. The mill stones could be adjusted at a short distance above the grinding surface so as not to break the pits of the olives that were being crushed.

The production of beer from malted barley and other cereals is also of very ancient origin, but its use was more largely confined to countries outside the Greco-Roman world and less is, therefore, known concerning the details of its manufacture.

Butter and Cheese.—The utilization of the milk of cows, goats, sheep, asses and other farm animals for the manufacture of butter and cheese has been practiced from primeval times. Butter according to PLINY (Book 28, Chap. 35) was made "from milk by merely shaking it to and fro in a tall vessel with a small orifice at the mouth to admit the air." This appliance for separating butter-fat from milk corresponds to the modern churn. Cheese was made in a variety of forms by coagulating milk with rennet, and compressing the curd into cakes after the addition of salt and flavoring

substances. In some cases the flavor of the cheese was heightened by smoking (PLINY, Book 11, Chap. 97).

Preservation of Foods and Forage.—The preservation of perishable food and forage for winter use was practiced by man at a very early period. Removal of excess moisture by drying was the method usually employed. PLINY is one of the earliest writers to call attention to the danger of spontaneous combustion in the curing of grass for hay (Book 18, Chap. 67):—

"When the grass is cut it should be turned towards the sun and must never be stacked until it is quite dry. If this last precaution is not carefully taken, a kind of vapor will be seen arising from the rick in the morning and as soon as the sun is up it will ignite to a certainty and so be consumed" (*loc. cit.*, Vol. 4, p. 92).

In addition to drying, perishable foods were preserved in ancient times by smoking, salting, and steeping in must, wine, vinegar or oil. The benefit of excluding dirt and air seems also to have been realized as in the following passage from PLINY regarding the preservation of cabbage (Book 19, Chap. 41):—

"It will keep green and fresh, during a long voyage even, if care be taken not to let it touch the ground from the moment that it is cut, but to put it into oil-vessels lately dried, and then to bung them so as to effectually exclude the air . . . Nitre (*i.e.*, natron), too, preserves the greenness of cabbages when cooked, a result which is equally ensured by the Apician mode of boiling, or in other words, by steeping the plants in oil and salt before they are cooked" (*loc. cit.*, Vol. 4, p. 187).

Agricultural Analysis:—Ancient science, although extremely weak upon the analytic side, possessed a few methods for determining the properties of agricultural products. The earliest of such methods was the use of simple sense perceptions such as those of taste, smell, color, feel, brittleness, etc. The quality of soils, as already mentioned, was judged by observing the character of native vegetation and by the properties of color, texture, odor and taste. The ancients, guided by such perceptions, were unquestionably better judges of the quality of many articles than are we today. PLINY (Book 15, Chaps. 32–3) enumerates no less than thirteen different flavors belonging to fruits and juices and his classification is so detailed that the translator is at a loss for suitable terms with which to express the meaning. Professional tasters were in demand during the early days of the Roman empire to determine the quality of wines and notwithstanding the present advanced chemical knowledge of the many esters which give wines their characteristic bouquet, the final criterion in the judgment of a wine, now as in the days of PLINY, is the evidence of a skilled taster.

But the ancients had many other means of examining their agricultural commodities than those of visual appearance, taste and smell, and some of these deserve mentioning as they mark the first beginnings of agricultural chemical analysis. A good illustration of such tests is given by PLINY in his description of balsam, an agricultural product of great value in Roman times (Book 12, Chap. 54):—

"As to the tears of balsam, the test of their goodness is their being unctuous to the touch, smell, of a somewhat reddish color, and odoriferous when subjected to friction. That of second-rate quality is white; the green and coarse is inferior, and the black is the worst of all; for, like olive oil, it is apt to turn rancid when old. Of all the incisions, the produce is considered the best of those from which the liquid

has flowed before the formation of the seed. . . . Balsam, in a genuine state, should be quite hard, but when it is contaminated with gum a brittle pellicle forms upon it. The fraud can also be detected by the taste and when placed upon hot coals it may easily be seen if there has been any adulteration with wax and resin; the flame too, in this case, burns with a blacker smoke than when the balsam is pure. . . . In addition to these various tests, a drop of pure balsam, if placed in luke-warm water will settle to the bottom of the vessel, whereas, if it is adulterated, it will float upon the surface like oil, and, if it has been drugged with metopion or ammoniacum, a white circle will form around. But the best test of all is that it will cause milk to curdle and leave no stain upon cloth" (*loc. cit.*, Vol. 3, pp. 150-1).

This passage, of which many others of a similar character might be quoted, shows that observations of a crude character were practised by the ancients in grading, and in testing the quality of their agricultural products. Various modifications of the flame test are mentioned by PLINY and DIOSCORIDES. In some cases the color and smell of the smoke were observed, in others the color of the flame, or the property of decrepitating.

The formation of a white ring, as described by PLINY, will recall to the chemist the numerous ring tests which are used in the laboratory at the present day, as well as the host of color reactions employed in the examination of foods and drugs. Color reactions of all kinds were used extensively by the ancients. PLINY (Book 35, Chap. 52) mentions for example that pomegranate juice and tincture of nut galls are colored black by alum. Authorities differ somewhat as to the exact nature of the compound that was called *alumen* by the Romans and *συνπηρία* by the Greeks, but all seem agreed that iron sulfate was present. The test described by PLINY is, therefore, nothing but the familiar tannin reaction with salts of iron.

An interesting modification of the nut gall test, mentioned by PLINY, consisted in the employment of strips of papyrus, which had been previously steeped in an infusion of nut galls (Book 34, Chap. 26). This is perhaps the earliest mention of the use of test papers.

The student of the history of science is often surprised not only at the acuteness of the ancient observations but also at the failure of men to follow the obvious clew to an important discovery. PLINY, for example (Book 23, Chap. 31), mentions the fact that

"the lees of wine are so extremely powerful as to prove fatal to persons on descending into the vats. The proper precaution for preventing this is to let down a light first, which so long as it refuses to burn, is significant of danger" (*loc. cit.*, Vol. 4, p. 482).

This ancient precaution against the dangers of asphyxiation is still posted in some modern wineries. History is silent as to the name of the man who first proposed so valuable a test. It was perhaps discovered by someone with a lighted lantern in attempting to rescue a comrade who had been overcome with carbon dioxide. The practical value of the test was long ago recognized, but thousands of years had to pass before anyone thought of establishing a possible analogy between human respiration and the burning of a candle. Even if this thought had occurred to PLINY the time was not ripe for subjecting it to an experimental test. The science of chemical analysis had to be developed before this and other problems of agricultural chemistry could be solved.

Quantitative methods of analysis were developed by the ancients to but a very limited extent. The celebrated Greek mathematician and experimenter ARCHIMEDES (287–212 B. C.), by his method of displacement, was the first to apply the principle of specific gravity to analytical problems. The method with various modifications seems to have been extended after the time of ARCHIMEDES. PLINY, in fact, alludes to the use of some form of balance (*statera*) for testing the purity of water (Book 31, Chap. 23). The Greek alchemist SYNESIUS (about 373–414 A. D.), in a letter to his teacher HYPATIA, describes minutely the construction of an areometer, which in appearance and use was the prototype of the modern specific gravity spindle. It was employed no doubt in the examination of water, wine, and other liquid products.

Relations of Medicine and Pharmacy to Agricultural Chemistry in Ancient Times: — Physicians because of their interest in the nutritive, dietetic and medicinal value of plant and animal products have been most prominent in the development of agricultural chemistry from earliest times down to the present. Much could be written about the influences exerted by the ancient medical schools of HIPPOCRATES and GALEN upon topics related to nutrition, sanitation and hygiene that are now considered in many treatises upon agricultural chemistry. Pharmacists also in their study of the roots, leaves, flowers, and seeds of plants and of their gums, oils, juices, resins and other exudations have contributed much to the chemistry of plants and especially to the development of apparatus and methods for their chemical examination.

The oldest manuscript which mentions the oily, tinctorial, aromatic, flavoring, narcotic and other principles of plants is the Ebers papyrus, an ancient Egyptian medical manuscript of about 1550 B. C. now preserved in the library of Leipsic University. The preparation of medicines from various plants by processes of drying, pulverizing, extracting, heating, filtering, pressing, clarifying, etc., described in this papyrus, indicates a high development of laboratory technique at this early age and as this papyrus refers to still earlier compilations it seems reasonable to suppose that knowledge of this kind in Egypt dates back to before 3000 B. C. Many recipes for preparing medicines, dyes, alloys, etc., compiled by the ancient Egyptian scribes, were transmitted to succeeding generations and some of these, translated in later times into Greek, no doubt were included in the collection of recipes contained in the Greek Papyri of about 300 A. D. now preserved in Leyden and Stockholm.

DIOSCORIDES OF ANAZARBA, a Greek physician of the first century A. D., wrote a treatise entitled "Περὶ Ὑλῆς Ἱατρικῆς" or in Latin "De Materia Medica," which describes "the preparation, potency, and testing of drugs" of plant, animal and mineral origin. A beautiful manuscript of this work of about 512 A. D. with many colored illustrations of different plants, is preserved in the National Library of Vienna. In this work DIOSCORIDES, who was a physician attached to a Roman army, has included not only his extensive observations in different parts of the Mediterranean world but also many of the recipes that had been handed down from previous times. He describes the characteristics, nutritive properties and physiological

action of the roots, fruit, seeds, etc., of numerous wild and cultivated plants and also of various vegetable juices, oils, resins, gums, and other products. The dietetic values of lard, tallow, marrow, butter, cheese, rennet, and other animal products are discussed. Fruits of the melon class are characterized as cooling, and spices, such as mustard, pepper and ginger, as warming — an old basis of classification that was followed as late as 1704 by LOUIS H. LEMERY in his "Treatise of Foods".

DIOSCORIDES gives some attention also to chemical processes. The following translation of his method for preparing *Fuligo Thuris*, by the

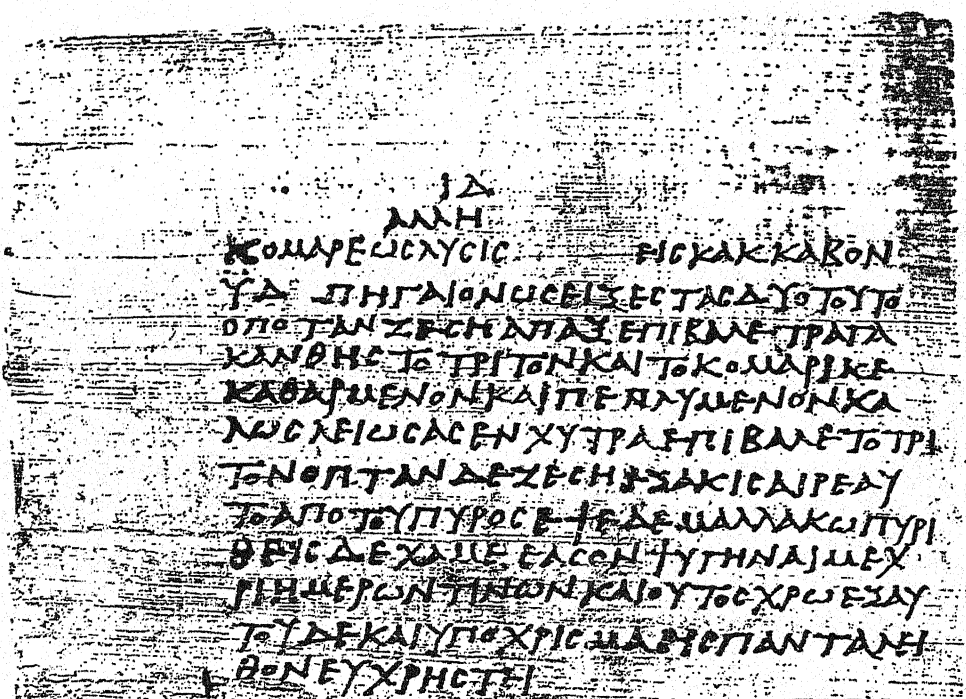


FIG. 6. — Greek papyrus recipe of about the early fourth century A.D. for preparing a vegetable dye. — "Heat two pints of spring water to boiling. Add a third part of gum tragacanth and a third part of pure washed komari previously pulverized, etc." Illustration from *Papyrus Graecus Holmiensis* by O. LAGERCRANTZ.

carefully controlled carbonization of frankincense, is illustrative of the laboratory technique of his time: —

"Soot of frankincense is made as follows: Taking a grain of frankincense with a pair of tweezers, light it at a lamp and place it in a new hollow earthenware vessel. Then cover it with a bronze dish, hollow within, perforated with holes in the middle, and carefully wiped clean. Then put on one side of it, or on both, little stones of four fingers height in order that it may be seen plainly if it is burning and that there may be a place always for depositing other grains before the first grain is extinguished. Continue doing this until you think you have collected sufficient soot. Always keep the outside of the bronze dish wet with a sponge dipt in cold water, for thus all the soot is deposited thereon not being overheated, otherwise it falls off because of its lightness and becomes mixed with the ash of frankincense. Scrape off the first deposit

of soot and repeat the process as often as you desire, removing to one side the ash of the frankincense that has been burned.

"It has the power of appeasing inflammation of the eyes, of checking fluxes, of healing sores, of filling cavities and of subduing cancerous growths" (WELLMAN, I, p. 64).

The "Materia Medica" of DIOSCORIDES was much read and in the sixteenth century gave rise to the publication of several commentaries. The first Latin translation was printed in 1478. The original Greek text was published by ALDUS in 1499. A Latin translation, with exhaustive illustrated commentary by P. A. MATTHIOLUS, was published at Venice in 1554.

Conclusion:— Without making further citations from ancient authors regarding the crude beginnings of what is now termed agricultural chemistry we may summarize by saying that this science was developed in Greco-Roman times much more strongly upon the practical than upon the theoretical side. The art of agriculture, based upon centuries of observation and experience, had developed to a high state of efficiency, but scarcely any progress had been made in reaching a true scientific explanation of the chemical, physical, and biological processes that were involved. The Greek love for speculation had given rise to numerous physical theories, of which the doctrines of the atomic school stands out as the highest attainment. But the test of the validity of the rival systems of ARISTOTLE and DEMOCRITUS could only be established by experiment and for this the world of science had to wait over a thousand years after the downfall of the Roman Empire.

Meanwhile the speculative ideas of ARISTOTLE with their insistence upon the mutations and transformations of the four hypothetical elements—earth, air, water, and fire—continued to retain the ascendancy in all branches of natural science. These elements and their attached qualities of the dry, wet, cold, and warm were made the basis of a quasi-chemical theory of agriculture. The warmth of the animal body and the production of heat by fermenting vegetable matter were attributed to the presence of an inherent fire. The residue of ash produced by the incineration of animal and vegetable materials was held to be a demonstration of their containing the element earth and the expulsion of volatile gases and moisture on ignition of these substances was regarded as a proof of their containing fire, air and water. Abnormalities in the proper balance of the four elements were supposed to explain the sterility of soils and the diseases of plants and animals. If the element fire was in excess, for example, the animal had fever, the hay-stack caught fire spontaneously and the soil burned up the vitality of seeds.

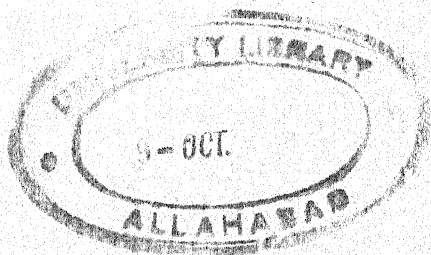
The different characteristics of soils, plants, and animals were explained by their variable content in earth, water, air and fire, while the growth, death and decay of living organisms were attributed to a gain or loss in one or more of these four supposedly essential elements. An excess of any one of these was thought to give a substance a preponderating share in the properties of hot, cold, dry, or wet, as the case might be. The functions of the animal organism were thus attributed to the four humors, each of which was produced from foods of the requisite elementary property, those

of a warm nature, such as mustard, being more productive of bile, and those of a cold nature, such as melons, being more productive of phlegm. Modifications of this ancient philosophy of nutrition had followers well into the eighteenth century. In the same way that the humors were supposed to be produced by particular vegetables, the latter were held to require for their growth a similar adaptation of soils, those that were warm being necessary for the plants that generate bile and those that were cold being required for the plants that give rise to phlegm. Such, in substance, was the theory of agricultural chemistry which under the influence of scholasticism prevailed in European countries between the fifth and the fifteenth centuries.

Further progress could not be made until after the overthrow of the old speculative philosophy and for the initiation of this reform the world of science is chiefly indebted to PARACELSUS.

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Chapter II

AGRICULTURAL CHEMISTRY IN THE ALCHEMICAL AND IATROCHEMICAL PERIODS

Philippus Theophrastus Paracelsus (1493-1541):—"Am ersten ist der Yliaster getheilt worden, der dann nichts ist und hatt geben die 4 Elementen." With these words in quaint archaic German begins the book of the Philosophy of PHILIPPUS THEOPHRASTUS PARACELSUS.

"In the beginning the Yliaster (*i.e.*, Primeval Chaos), which was then nothing, was divided into the four elements . . . into air, which is the heaven that embraces all things; into fire which is the firmament that produces day and night, cold and heat; into earth which yields all kinds of fruits and provides a foundation for our feet; and into water from which are derived all minerals and half the food of living beings" (HUSER, Vol. 8, pp. 55, 57).

This passage might seem to indicate a continuance of ancient traditions, yet a most abrupt and definite break with the scholastic system had occurred.

PARACELSUS was born in Einsiedeln in Switzerland on November 10, 1493, and in his early youth had come to realize the barren results of the old philosophy with its emphasis upon the value of the so-called liberal arts, as contrasted with the servile or useful ones. Accordingly he forsook the university, with its empty discussions of theories and definitions, and departed for the mines of Tyrol where he could mingle with workmen and obtain a first-hand acquaintance with the world of reality. His experience in the mines confirmed his belief that true knowledge was to be gained not by scholastic disputations but by association with those who actively participated in the operations of nature. He, therefore, made a pilgrimage over much of Europe to widen his observation and experience.

About 1527 PARACELSUS began to lecture upon medicine at the University of Basel. He indicated at once his break with tradition by burning the books of GALEN and AVICENNA before his students. This act, coupled with his lecturing in German instead of in Latin and with his outspoken attacks upon the adherents of the old philosophy, aroused such opposition that he left the university and devoted the remainder of his days to a wandering life. He settled finally in Salzburg but his body had been so weakened by an irregular mode of life, that he died there soon afterwards, following a short illness, on September 24, 1541.

In the brief intervals of his sojourns in various cities PARACELSUS wrote several of the treatises that bear his name, but most of his works were in the handwriting of his disciples to whom they had been dictated and who left them in a state of considerable disorder. This confusion was further increased by the appearance of many spurious works that were falsely attributed to PARACELSUS. Finally JOHN HUSER, a doctor of medicine, made a critical examination of all the manuscripts and published those which he considered to be genuine in a ten volume edition at Basel in 1589-91. It is to this edition that the following citations and translations refer.

The character of PARACELSUS presents a strange mixture of contradictions—an earnest purpose for the discovery of new truth upon the one

Ander Theil
Der Bücher vnd Schrifften des
Edlen/ Hochgelehrten
vnd Bewehrten **PHILOSOPHI**
vnd **MEDICI,**

PHILIPPI THEO-
PHRASTI Bombast von Ho-
henheim/ **PARACELSI**
genannt:

Jetzt auffs new auß den Originalien / vnd
Theophrasti eigner Handschrift/ soniel derselben zu
bekommen gewesen/ auffs treulichst vnd
reiffigst an tag geben:

Durch

IOHANNEM HUSERVM BRISGOIVM
Churfürstlichen Cölnischen Rath vnd
MEDICVM,

Dieser Theil begreiffi fürnemlich die Schrifften/ in denen die
Fundamenta angezeigt werde/ auff welchen die Kunst der rechten Arzney
stehe/ vnd auß was Büchern dieselbe gelehret werde.
Den Catalogum dieser Schrifften wird
die vierde Pagina anzeigen.

*Adiunctus est I N D E X Rerum & Verborum accu-
ratis. & copiosissimus.*

Getruckt zu Basel durch
Conrad Waldkirch.

ANNO M. D. LXXXIX.

FIG. 7.— Title page of Vol. 2 of HUSER's Edition of the Works of PARACELsus.
Basel, 1589.

hand and a belief in crude medieval superstitions upon the other. The boastful arrogance, which made him so many enemies, is indicated in the following passage from the prologue of his "De Tinctura Physicorum":—

"The monarchy of all arts is conferred on me THEOPHRASTUS the Prince, in possession of which I, chosen by Almighty God, will suppress every fantasy and fictitious work of pretenders, whether ARISTOTLE, AVICENNA, MESUE or any one else, with all their followers. My theory proceeds from the light of nature and because of its constancy can never be overthrown. . . . Practice following next will be manifested by incredible signs and wonders so that workmen and common people will understand how the art of THEOPHRASTUS triumphs over the bunglings of the Sophists although their incompetence be fostered and protected by papal and imperial privileges" (HUSER, Vol. 6, p. 364).

PARACELSUS, by breaking with the orthodox scientific traditions of ARISTOTLE, GALEN, and AVICENNA and by forsaking Latin, the established language of science, for the common speech of everyday life, initiated a revolution in both medicine and chemistry and with him we may date the commencement of a new era in the pursuit of science. He has been called a vain sensational quack, a greedy impostor and an ignorant pretender; he possessed many of the faults and vices of his time; his works teem with non-sensical references to astrology, necromancy, magic and other superstitions of the Middle Ages; he discoursed upon the Yliaster, the microcosm, the quintessence, homunculi, amulets, and salamanders. Yet he had natural gifts of a high order and a forceful personality by which he stimulated men to forsake outworn traditions and to think for themselves. His posthumous works, published in ten quarto volumes of over five thousand pages (partly genuine and partly spurious), remain as evidences of his industry and influence. Although a believer in transmutation he taught that the main object of chemistry was not to change base metals into gold but to make medicines for the cure of diseases. He thus became the founder of the iatrochemical or Paracelsian school of medicine, several of whose representatives made important contributions in the applications of chemistry to agriculture and the other useful arts.

Although adhering to the Aristotelian doctrine of the four elements PARACELSUS held that these so-called basic constituents of the material world were not simple substances but mixtures of the three principles—sulfur, mercury, and salt—by which were meant not the common substances of these names but their potential qualities of combustibility, fluidity, and solubility. He made these so-called principles the basis of his iatrochemical system. "If any one wishes to read and understand my philosophy," he proclaimed, "let him know that sulfur, mercury, and salt are the best and surest guides of the physician." PARACELSUS also made his three principles the basis of a new system of plant and human nutrition, as indicated by his treatise

"On Salt and its Nature"

"God has elevated and forced man to such a height that he can in no wise live without salt but must have it in his food and all his nutriment. He is compelled thereto by necessity and the reasons for this I will now explain:

"Man consists of three things—sulfur, mercury, and salt. And everything that exists consists of these three things neither more nor less. These are the body of each single thing whether endowed, or not endowed, with sense. Now since man is divided into species, he is subject to putrefaction nor can he avoid decay except

in so far as God has protected him with an incarnate balsam which is one of the three principles namely salt. It is this balsam that protects man from decay for where there is no salt nor saltiness in that place decay occurs. For just as dead meat is protected by salt from decaying so the salt, with which God by nature has infused us, preserves our bodies from putrefaction. It is then agreed that man consists of three principles of which salt is the one that protects the body, in which it was implanted, from decay. Since now the *prima Conditio* or first substances, are composed of three principles, it follows that they must be maintained by nutriment. So also every vegetable of the earth must give nutriment to the three things of which they consist. If they fail to do that the *prima Conditio* perish and die in their three species. These nutriments are earth and rain, that is the Liquor, each of the three parts of which nourishes its own kind—sulfur for sulfur, mercury for mercury, and salt for salt, for Nature contains these, one with the others. From this Liquor, which is the nutriment of natural things, natural salt is concocted.

"From this it is evident that man also must nourish himself in the same way; that is his sulfur must have its nutrimental sulfur, his mercury its nutrimental mercury and his congenital salt its nutrimental salt, in order that from these three man may be sustained in his three species. Whatever burns is sulfur, whatever is moist is mercury and that which is the balsam of these two is salt. The nutrition of man depends upon the fact that he must eat combustible food to sustain his sulfur, moist food to sustain his mercury, and salt for the salt of his nature. If this order is not maintained that species in the body which is deprived must perish and if one perishes the others perish also. The order must therefore be maintained. The superior schools of learning, however, know nothing of this philosophy, just as they know nothing else nor are capable of knowing" (HUSER, Vol. 7, pp. 141-2).

The obscurities of this passage when interpreted in modern language mean simply that vegetables receive from the soil and rain for their nutriment organic constituents (sulfur), water (mercury) and mineral matter (salt), without any one of which they are unable to subsist. Man also requires the same elements of nutrition, organic or combustible food (*brennende Speiss*, i.e., calories), water and mineral matter. If any one of these is lacking, the body suffers although the other two necessary nutrients may be present (*zergeht Eins so zergehen auch die andern*). We note here a dim recognition of the "law of the minimum" announced three centuries later.

The conception of three principles was no advancement over the old hypothesis of four elements. It merely served as a rallying point for those who wished to break with an outworn tradition.

Earth, the fruit-bearing element, according to PARACELSUS, varies in productivity. It may be barren or one kind may be adapted to one crop and another kind to another. These differences, he held however, were not due to the soil itself, which was supposed to be uniform in character, but to the weather which may either promote or impede the growth of vegetation (HUSER, Vol. 8, p. 99).

Plants and animals, according to PARACELSUS, can be separated into their proximate constituents and these by further decomposition can be resolved into varying mixtures of their original elements. In his book "De Separationibus Rerum Naturalium" PARACELSUS mentions the products obtained from plants and animals and the different chemical processes by which these separations are accomplished.

"Plants in their separation yield water, oil, juice, resin, gum, tar, electuaries, powder, ashes, mercury, sulphur and salt. Animals in their separation yield water, blood, flesh, fat, bone, hide, body, hair, mercury, sulphur, and salt, etc. Whoever wishes to boast of a perfect separation of all such natural things requires great expe-

rience and complete understanding of all natural things; he has need besides of a skilled alchemist that he may know what is combustible and incombustible, what is fixed and what is volatile, what is fluid or solid or what thing is more important than another. He must besides have knowledge of each natural color, smell, acidity, astringency, feel, bitterness, sweetness, grade, complexion and quality.

"In addition he should know also the steps of separation, such as distilling, resolving, putrifying, extracting, calcining, reverberating, subliming, reducing, coagulating, pulverizing and decanting. In distillation water and oil are separated from all corporeal things. In resolution metal is separated from ore, one metal from another, salt from other things, fatty from lean, and light from heavier. In putrefaction the pure is separated from the impure, and the rotten from the sound. In extraction the spirit and quintessence are separated from their body and the pearly from the coarse. In reverberation everything that is colored, odorous, combustible, wet, fat, fugitive and unstable is separated. In sublimation the fixed and volatile are separated from each other, the spiritual from the corporeal, sulphur from salt and mercury from salt. In reduction the liquid is separated from the solid, the metal from its ore and slag, and the fat from the non-fat. In coagulation the wet is separated from the moist and water from earths. In pulverization dust and sand are separated from each other, ashes from lime, and the mineral from the vegetable and animal. And all the powders that differ in weight are separated by jaculation, that is by tossing and letting fall just as chaff is winnowed from grain. In decantation ashes and sand are separated from each other, the ore from its metal, the heavy from the lighter, the vegetable and animal from the mineral, sulphur from mercury and salt, and salt from mercury" (HUSER, Vol. 6, pp. 316-7).

The method recommended by PARACELUS for the separation of oleaginous substances into their primary elements is thus described in Book 3 of his *Archidoxis*:

"In the class of oleaginous substances are all oils, wood, roots, seeds, fruits, etc., which have a combustible nature and are fit for burning. For the analysis of these there are two procedures, one for the oleaginous substances and one for the pure oils. For oleaginous materials proceed as follows: Grind or shred the substance as finely as possible, in whatever way you can; wrap it up in a cloth and place it in horse manure until it has entirely putrified, which occurs sooner with one substance than with another. Put the putrified substance in a retort and pour over it low grade spirits to a depth of four fingers; then distill off on a sand-bath everything that will go over. All the elements except earth go over as you will know by the colors—first the spirits, then air, then water, then fire and finally earth remains at the bottom. As for pure oils, these do not require putrefaction but are distilled without additions. Proceed in the same way with resinous substances which yield liquid products such as pitch, tar, turpentine, gum and the like" (HUSER, Vol. 6, p. 18).

The passages just quoted indicate that chemical laboratories in the time of PARACELUS were well equipped with different kinds of apparatus for performing a large variety of operations. The art of plant analysis is seen here in its early infancy, but progress was slow and the processes described by PARACELUS underwent very little improvement during the next two centuries.

Even more crude than the conceptions of PARACELUS regarding the composition of plants were his views pertaining to animal chemistry. According to the doctrine of PARACELUS and his early followers digestion and other functions of the human and animal body were regulated by an inner transmuting vital agency variously designated as the *archeus* or alchemist. The functions of this inner regulator of digestion are thus described by PARACELUS in Chapter 7 of his treatise "*De Ente Venini*":

"That we may give you an explanation of the alchemist, understand that God has given each creature its being and what is pertinent thereto not for the purpose of self-regulation or the like but for the purpose of utilizing the sustenance necessary for its existence and which sustenance is accompanied with poison. Each creature has in its body an entity which separates this poison from that which the body assimilates. This entity is the alchemist, so called because he employs the art of alchemy. He separates the bad from the good, he changes the good into a tincture, with which he tinges the body with life. He regulates what is subject to Nature; he tinges it so that it becomes blood and flesh. This alchemist dwells in the stomach, which is his

der zu formieren. Allein der Spiritus Salis der thut das/ die-
weil vnd er die materiam lapidis findet/ so arbeit er darinn wie
ein hie von der Sonnen/ die ist[wie] Spiritus Salis/ so sie finde
ein mucilaginem, viscū &c. so trucknet es auß: vnd was es ist
in der coagulation/ dz wirt es/ souil jhr ampt ist. Darumb aber
dz sie nit Spiritus Salis ist/ darumb so mag sie Stein materien
nit zu Stein machen: Also auch andere Steinen/ dann do ist
kein Stein der hie theil hab / allein der Spiritus salis der bringe
Stein materiam in Stein/ das ist/ er fürts in sein vltimā ma-
teriam. Als ein exempel mit der speiß/ die mag kein andere
hie/ sewr oder digestio in sein vltimam materiam bringen/ als
allein der Magen der Menschen der hatt den gewalt. Darinn
werden vil jrung gefunden in der Vulcanischen art/ die da
mit des weges derselben vltima materia zubringen. Vil seind/
die da feulen/ aber darumb ist nit via vltimæ materiæ/ sonder
ein Irnsal. Darumb so thuts die hie im leib nit/ v Spiritus Salis
v thuts. Wer weiß wie er ist/ allein der Philosoph⁹ weiß/ nit v
Arzt. Diweil nun die Philosophy dz also außweist vñ also v
Arzt darbey bleiben muß/ so laß ich dasselbig hie bleiben: Vnd
melde weiter von der scheidung wie sie sich begibt in den nach-
folgenden/ wie also auß jhr die genera Tartari angehn/ vñ wie
sie durch den spiritum Salis dahin gebracht wirt/ vnd das also.

FIG. 8. — Specimen of mixed German and Latin text from Book III, Treatise II of the *Paramirum* of PARACELSUS. (Vol. I, p. 151, HUSER's Edit., 1589).

instrument, where he cooks and works. Moreover understand this also. Man when he eats meat eats that in which are both poison and good but in eating he thinks it is all good whereas among the good are concealed poison and the bad which are not good. As soon as the food, which is flesh, comes into the stomach the alchemist is at once there and proceeds to digest it, rejecting that which is not healthful to the body into a special place, in order that the good may go where it belongs. That is a law of the Creator. In this way the body is maintained and acquires nothing poisonous from what it eats. The poison is thus eliminated by the alchemist who receives no recompense on the part of man. Such is the virtue and power of the alchemist in man" (HUSER, Vol. I, pp. 28-9).

The modern student in reading PARACELSUS must bear in mind that he had at his command no chemical terminology and that to make his subject intelligible he was obliged to use such allegorical illustrations as could be comprehended by the men of his time. The alchemistic controller of nutrition, which he pictures, is simply a medieval personification of what are now called ferments or enzymes. He emphasizes the fact that this digestive agency was different in different animals:—

"The peacock eats snakes, lizards and newts. These creatures, perfectly healthy in themselves, are poisonous to other animals with the exception of the peacock. The reason for this is that its alchemist, unlike the alchemist of other animals, is so subtle that it sharply separates poison and good from what is harmless to the peacock. Therefore remember that each animal has its own peculiar food and its own special alchemist for digesting it. The alchemist of the ostrich has the faculty of digesting iron (the stercus of nutriment) that is wholly unsuited for other animals. The salamander has fire, the Corpus Ignis, for its food for which it has its special alchemist. The pig has for its food dung which being a poison is therefore excreted from man by the alchemist of nature. Yet it is food for the pig because the pig's alchemist is much more subtle than the alchemist of man, and can separate food from dung which the alchemist of man was not able to do. For this reason pig's dung is not eaten by any animal. No alchemist is so exact and so thorough in utilizing its food as the pig's alchemist" (HUSER, Vol. I, p. 26).

Of such and similar character were the crude vitalistic conceptions of nutrition which prevailed until after the beginning of the eighteenth century.

Chemistry owes a great debt to PARACELSUS in that he emphasized the importance of experimentation. In a famous passage, frequently quoted, he compares the toiling chemical practitioners with the foppish adherents of the speculative schools:—

"They do not go idly about in gorgeous suits of satin, silk and plush, with gold rings on their fingers, silver daggers at their sides and white gloves on their hands, but they tend patiently to their work at the fire day and night. They do not go promenading around, but seek their diversion in the laboratory, wearing rough leather garments, with aprons on which to wipe their hands, and thrusting their fingers amongst the coals into dirt and grime and not into gold rings. They are as sooty as a blacksmith and charcoal burner and therefore care little for display" (HUSER, Vol. 6, p. 323).

Many applications of modern chemistry can be traced back to the writings of PARACELSUS. The concentration of alcoholic beverages by freezing out the excess of water as ice is a process that is proposed from time to time in modern chemical literature. It is thus described by PARACELSUS in Book 6 of his *Archidoxis*:—

"Preparation of the Magisterium Vini"

"Take wine, the oldest and best that you have, and of such color and taste as you prefer; pour into a glass until it is a third full, seal hermetically, place in a putrifier of warm horse manure and allow to remain four months without letting the warmth escape. At the end of this time expose it in winter where the cold is most severe and let it stand there for a month that it may be frozen throughout. In this way the cold forces the *spiritus vini* to the centre of the wine, the substance of the wine and phlegm being thus separated. That which is frozen reject, but what is not frozen is the *Spiritus Vini* with its substance. Remove this, put in a pelican and let it digest on a sand bath for a short time at moderate heat. The product thus obtained is the *Magisterium vini*" (HUSER, Vol. 6, pp. 67-8).

PARACELSUS had the fiery temperament of the prophet and crusader. He prophesied the coming of an alchemistic messiah, ELIAS the Artist

(HUSER, Vol. 6, p. 370), who would reveal all the hidden mysteries of chemistry, and this expectation persisted for over a century after his death, finding its way even to seventeenth century New England. Yet while awaiting the arrival of this expected ELIAS, the followers of PARACELSUS were bidden to put their faith in experience.

"Let no one wonder", he declared, "at what we write. For although our path runs contrary to the old course it is directed by Experience who is mistress of all things and by whom all things are to be proved and made clear" (HUSER, Vol. 6, p. 8).

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Bernard Palissy (1510-89):— In the development of every science, there appear at long intervals certain men of rare intellect and vision who in their outlook have advanced so far beyond their contemporaries that they seem to have been born centuries before their time. Such a person was the French craftsman and investigator, BERNARD PALISSY, a self-taught man who, taking observation and experience as his only guides, cast loose from tradition, alchemy and the teachings of speculative philosophy. He was a younger contemporary of PARACELSUS but to turn from the books of the latter with their accounts of basilisks and other medieval superstitions to the pages of PALISSY is like a leap from the Middle Ages into modern times. PALISSY like PARACELSUS abandoned Latin for the vernacular and we see in his antique French, as in the crude German of PARACELSUS, the struggles of a new medium of scientific expression.

Although it was in the field of ceramics that the chief contributions of PALISSY lay, his study of the earths, clays, glazes, salts and other materials of his art caused him to investigate the nature of stone, soils, and fertilizers. He has been called the early founder of agricultural chemistry and the designation is not wholly unmerited when it is considered that PALISSY's views upon some phases of the subject anticipated the work of three centuries later.

The following extract upon manure is taken from the "Récepte véritable" of PALISSY (1563), a practical essay in economics, written to inform his

countrymen how they can conserve and increase their national resources. The essay is in the form of a dialogue between PALISSY and an imaginary friend:—

Palissy—“Manure is carried to the field for the purpose of restoring to the latter a part of what had been removed. In sowing wheat the planter hopes that each seed will produce several, but that is not possible without taking something from the soil. If a field has been planted several years, its substance has been carried off in the straw and grain. Therefore it is necessary to collect the manure, dirt, trash and all the excreta of both men and animals, so far as possible, in order to return to each place the same substances that have been removed. That is why manures should not be exposed to the rain, because the latter, in percolating through, carries away the salt which is their principal substance and virtue.”

Friend—“Your statement is ridiculous and I know several people who laugh at you because you say there is salt in manure. Give me a good reason for believing this.”

Palissy—“There is no crop, whether good or bad, that does not contain some kind of salt and when straw, hay, and other vegetation have decayed, the water that percolates through them carries away the salt which they contained. Just as salted haddock, or other fish, when soaked for a long time lose all their salty substance and finally have no taste. In the same way manures lose their salt when they are drenched with rain.”

Friend—“If you should preach a hundred years, you would never make me believe that there is salt in manures or in all the different kinds of plants.”

Palissy—“I will now give you arguments that will make you believe it unless you have the head of an ass on your shoulders. You are familiar with saltwort—a plant that grows abundantly in the marshy soils of Narbonne and Saintonge. Now this plant when burnt gives a salty ash which the druggists and alchemists call alkali. It is salt from a plant. The fern is also a plant which on being burnt gives a mineral salt which glassmakers use with other ingredients for making glass as I will explain later when discussing this subject. Take also the case of the sugar cane from which sugar is made. It is a plant with a knotted stalk like a reed. Yet it is from this plant that sugar is derived which is nothing else than salt.

“It is true that all salts have not the same taste, nor the same virtue nor the same action. There are an infinite number of salts upon the earth. Because they have not the same taste, the same appearance and the same action is no reason for believing that they are not salt. I strongly affirm again that there is no plant nor kind of herb that does not contain some sort of salt; I declare also that there is no kind of tree which does not contain it, some more and others less; and what is more I will state that if fruits had no salt they would have no taste, virtue or aroma and could not be kept from rotting. . . .

“If I should write down all the examples that I might mention it would take too long. . . . Copperas, vitriol, alum, and saltpeter are salts. Unless all things had salt, they could not last but would quickly rot and perish. Salt preserves and keeps pork and other meat from becoming putrid. As the Egyptians knew who built great pyramids for protecting the bodies of their dead kings; in order to keep the latter from decaying they embalmed them with nitre, which is a salt and with certain spices which contain much salt. And by this means their bodies have been preserved without decaying even to the present time. . . .

“Have you not seen certain laborers when planting a field two years in succession, burn the trash or straw, after the wheat had been cut? In the ashes of this straw will be found the salt which it took from the soil and this salt on being returned to the field will improve its soil. The straw, when burned on the field, serves as manure because it restores the same substances to the soil which it took away. It is time that I finish my argument, for if you still fail to be convinced it would be foolish to cite other examples. Yet to prove our original proposition, that rain does actually wash away the salt from unprotected manure piles, I will give, as a final argument, an illustration that will answer for all.

“In the spring when laborers carry their manure to the field you will note that a little while before planting they will put the dung in piles or heaps and then somewhat later spread it over the whole field. But on the places where the piles were

situated they leave nothing of the manure which has been scattered here and there. Yet on these bare spots, where the piles have stood, you will see after the wheat has come up that it will be taller, thicker, greener and more luxuriant than in other places. From this you will easily see that it was not the manure which has done this, for it was spread elsewhere, but that it was because the rain, on percolating through the piles of manure to the soil, dissolved and carried with it certain of the salts that belonged to the manure. Similarly water, when it percolates through earth containing saltpeter, carries away the latter and the earth that remains behind is then useless for making saltpeter, for the water has removed it all. . . ."

Friend — "What should I do then to protect my manure from damage?"

Palissy — "If you wish to preserve your manure in the best way, dig a shallow cavity like a small pond, in a suitable place near your stables and pave it with stones or brick, using a mortar of lime and sand. Store your manure here until it is time to take it to the field. In order that the manure may not be injured by the rain or sun, cover it with a roof and then when seedtime comes you will carry it to the field with all its substance, the pavement of the cavity having retained all the liquid part of the manure which otherwise would have been lost and absorbed by the ground. You should also observe whether any clear liquid has drained from the manure to the bottom of the paved cavity. If so this liquid, consisting of urine, etc., which cannot be transported in the dung baskets, should be conveyed to the field in water-tight receptacles, like those used for carrying grape juice. I assure you it is the best and most salty kind of manure. Proceeding thus you will restore to the soil the same substances that have been removed by previous crops and which following crops will regain to their advantage" (PALISSY 1888, Vol. I, pp. 28-35).

The employment of marl for the restoration of worn out lands has been advocated by many modern writers upon agriculture. Some of them, however, have overlooked the fact that the practice is a very old one, having been discussed as we have seen by PLINY. PALISSY devoted a whole chapter upon "The Earth called Marl which is used as a fertilizer for barren fields in the regions where it is known — a matter of great importance to those who own estates" in his book of "Discours admirables. . . ." This essay is also in the form of a dialogue between Theory and Practice.

Theory, having recourse to an old belief which persisted until after the time of BOERHAAVE, maintained that it was the occluded elemental heat in the marl which promoted vegetation.

Theory — "We know that the reason why manure assists vegetation is because of its heat. If it is so with manure it is likely to be so with marl and lime. . . ."

Practice — "All that is nothing to the point. We know when hay and straw are wet with water that they will decay and this decay causes a considerable heat until the radical essence is all dissolved. When this has happened, the manure has no longer any heat. We know also that burnt lime-rock engenders fire which lasts until the pieces have cracked and crumbled when there is no more heat there. We know also that boiling water is hot as long as it is heated by the fire, but after it has been removed from the fire it is more subject to freezing than water which has not been heated. . . . It is, therefore, necessary to conclude, since the soil is benefited by marl for a space of ten to thirty years afterwards that it is not caused by the heat which is in it. . . ."

Theory — "I never saw a man so obstinate in his opinions as you. . . . If the heat of the marl, the manure and the lime is not the cause which promotes vegetation, tell me by what virtue it is that the marl can benefit barren soils" (PALISSY 1888, Vol. II, pp. 225-29).

But having demolished the old theory of a latent elemental heat as the explanation of the beneficial action of marl upon soils PALISSY, owing to the limited amount of chemical knowledge then available, could not be helped in this dilemma by his two guides observation and experience and so, contrary to his principles, he was obliged, as have all others in similar

cases, to resort to speculation. He conceived the idea of a so-called fifth element, or "generative water", which, although associated with ordinary water, was distinguished from the latter by peculiar life-giving properties and by its ability to become attached to the earthy particles of the soil which it condensed to marl. The fertilizing action of marl, according to PALISSY, is then due, not to its mineral matter, but to the generative water with which it was combined. When crops after the space of several years have withdrawn this generative water, the residue of exhausted marl is then entirely useless. (Quant les semences par l'espace de plusieurs années ont attiré l'eau générative, la terre de marne est inutile comme le marcq de quelque décoction.)

PALISSY after a long and useful life, devoted to the service of his king and country, was imprisoned during the persecutions of the Huguenots and, refusing to change his religion, died in a dungeon of the Bastille at the age of 79.

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Joseph Duchesne (1521?-1609):—One of the earliest advocates of the Paracelsian doctrines in France was JOSEPH DUCHESNE who was more generally referred to by later writers under his Latinized name, QUERCETANUS. He was a native of Gascony, studied medicine in Germany and then returning to France became court physician of HENRY IV. DUCHESNE was the author of numerous Latin works upon medicine and chemistry. In his "Materia Medica of the Early Philosophers" (Book 1, Chap. 3) he describes saltpeter and remarks, "In saltpeter is a spirit which has the nature of air and which cannot support a flame but does just the opposite." DUCHESNE gives no information about the preparation of this spirit which, if made by the ignition of charcoal and nitre would have contained carbon dioxide. While the description might apply to nitrogen it cannot be stated, as some writers seem to imply, that DUCHESNE had isolated this element.

Recognition from agricultural chemists is due to DUCHESNE from the fact that he was one of the first to mention gluten which he prepared by the customary method of working a paste of flour between the fingers under a jet of water. He describes it as "a tenacious, waxy, decidedly glutinous substance" (*substantia tenax, cerea, prorsus glutinosa*).

DUCHESNE accepted the Paracelsian doctrines of the three principles and of signatures. To the various superstitions that he adopted from PARA-

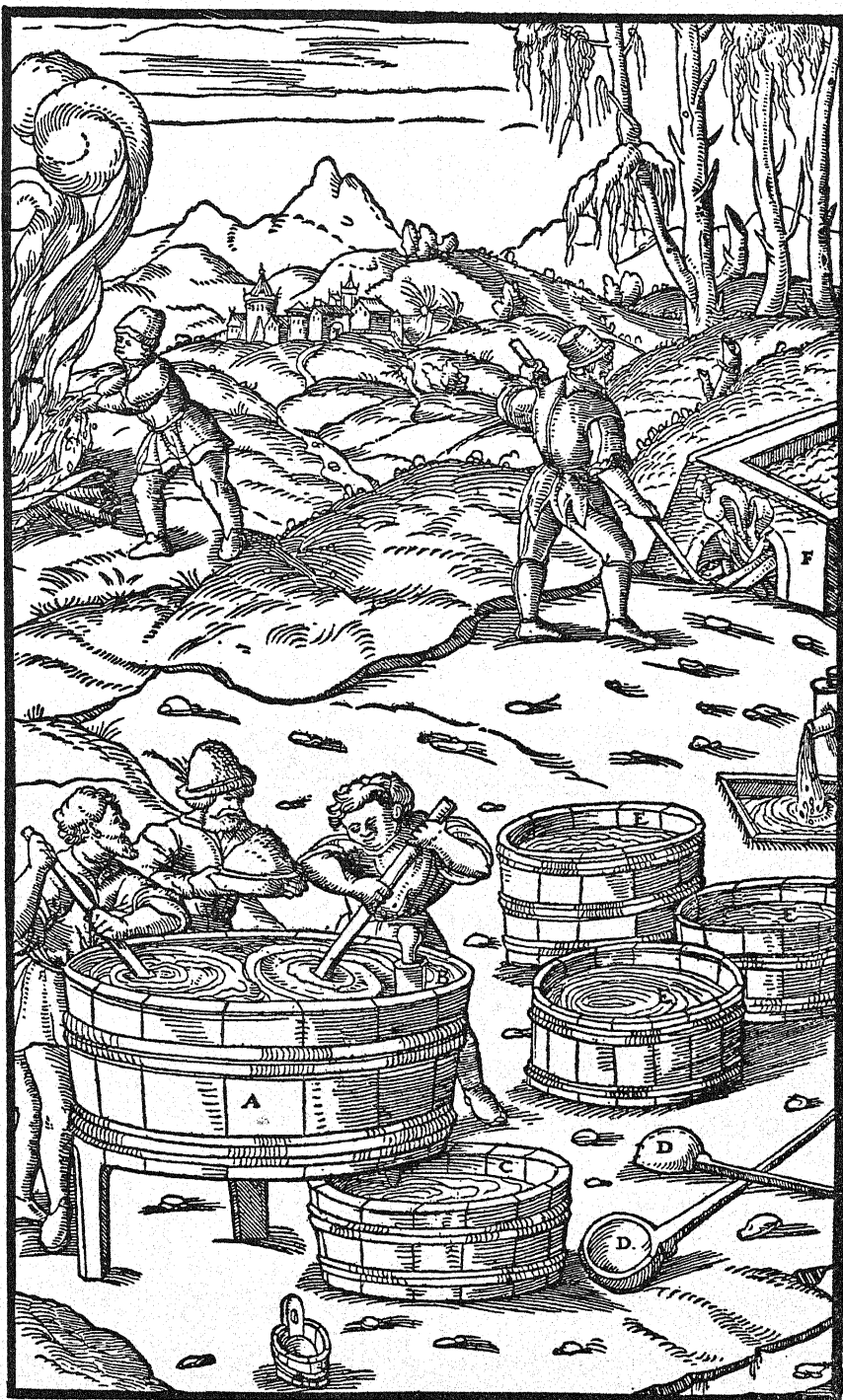


FIG. 9.—*Lixiviation of Wood Ashes for the Manufacture of Saltpeter.*—From the “*De Re Metallica*” of AGRICOLA. 1556. Edition of HERBERT CLARK HOOVER and LOU HENRY HOOVER, London 1912, p. 557.

CELSUS, DUCHESNE added a piece of credulity of his own invention which was that of palingenesis. In accordance with this strange conception it was held possible by chemical means to regenerate an entire plant from its ashes and reverberations of this alchemistic belief continued for nearly two centuries. Mention of the doctrine even crossed to early New England where it found its way into the "Magnalia" of COTTON MATHER who thus describes it:—

"QUERCETANUS, with a whole tribe of 'labourers in the fire' since that learned man, find it no easy thing to make the common part of mankind believe that they can take a plant in its most vigorous consistence and, after a due maceration, fermentation and separation, extract the salt of that plant, which, as it were in a chaos, invisibly reserves the form of the whole, with its vital principle; and, that keeping the salt in a glass hermetically sealed, they can, by applying a soft fire to the glass, make the vegetable rise by little and little out of its ashes . . ."

Much time was spent by overcredulous workers in plant chemistry two centuries and more ago to perform DUCHESNE's experiment of palingenesis but the efforts, like those of trying to transmute lead into gold, were never successful. It was held by some that the branching plant-like configuration of crystals, obtained by evaporating the solution of salts from the ash, was what DUCHESNE had in mind. Since the old writers were continually allegorizing it is possible that the doctrine of palingenesis was only a mystical statement of the law that a plant cannot grow to maturity unless it is supplied with the elements that are found in the ash of its species.

The ashes of plants and trees in this period began to acquire not only a speculative, but a practical significance owing to their employment in the manufacture of potash, lye, soap, glass, saltpeter, and other industrial products. The lixiviation of wood-ashes for the manufacture of saltpeter is shown in the accompanying reproduction of an old wood-cut from the "De Re Metallica" of AGRICOLA, published in 1556. With the founding of English colonies in the New World during the early seventeenth century the manufacture of potash from wood-ashes for exportation to Great Britain became an agricultural industry of foremost importance in North America until the War of 1812.

Francis Bacon (1561-1626):—The chief exponent of the art of making discoveries by experimentation was the famous English philosopher, Sir FRANCIS BACON, who, by means of his new systematized method of investigation, the *Novum Organum*, aimed to effect a complete regeneration of the sciences.

BACON was born at York House, London, on January 22, 1561. At the age of twelve he entered Trinity College, Cambridge, where he obtained his first acquaintance with the various natural sciences. His rise through the posts of barrister, solicitor, privy councilor, and lord keeper to that of lord chancellor was rapid, but during the busy period of these advancements he won even greater distinction as an essayist and philosopher. His celebrity rests chiefly upon his efforts to reform the methods of scientific inquiry by means of inductive observations combined with coöperative experimental research.

Like PARACELSUS, BACON scorned the pretensions of scholastic philosophy. He blamed especially ARISTOTLE for corrupting science with his logic

SYLVA
SYLVARVM:

OR,
A Naturall History.

IN TEN CENTURIES.

WHEREUNTO IS NEWLY ADDED
the History *Naturall* and *Experimentall* of
LIFE and DEATH, or of the
Prolongation of Life.

BOTH WRITTEN BY THE RIGHT
Honourable FRANCIS LO. Verulam
Viscount S^t ALBAN.

Published after the Authors death,
By WILLIAM RAVVLEY *Doctor in Divinity,*
one of his Majesties Chaplaines.

Hereunto is now added an Alphabetically Table of the prin-
cipall things contained in the ten Centuries.

The sixth Edition.

LONDON,
Printed by J. F. for William Lee, and are to be sold at the Great
Turks Head over against Fetter-Lane in Fleetstreet. 1651.

and for making the world to consist of categories. Like PARACELSUS also BACON recognized experience as the best teacher and emphasized the value of useful studies, such as were related to the farm, the kitchen, and the machine shop. But here the agreement ends for of the many critics of PARACELSUS the most severe was BACON who, departing from his usual calmness of expression, denounced him as a flagrant falsifier, pretender, and imposter. Yet strangely enough BACON did not object so much to the doctrine of three principles, the real spot of weakness in the system of PARACELSUS, as he did to the latter's methods of experimenting.

"His three principles," writes BACON, "might be received with some utility: as having a foundation in nature; but he is continually wresting them to every thing according to his great dexterity in delusion and imposture. . . . The sophists were only deserters of experience, but PARACELSUS has betrayed it; and subjecting the crude and personated evidences of things to rules of contemplation, and deriving the various alterations of substances from imaginary motions, he has thus endeavored to corrupt the fountains of science, and dethrone the human mind. At the same time, so far is he from understanding, or justly representing experience, that he has added to the trouble and tediousness in experimenting" (Works, 1818, Vol. XI, p. 269).

BACON's accusation that PARACELSUS "added to the trouble and tediousness in experimenting" might be applied, however, to himself for his famous system of the *Novum Organum*, which was designed for the purpose of facilitating the discovery of knowledge, was so intricately complicated and overloaded with axioms, instances, rules and other details of procedure that scientific research has never followed this part of the Baconian method. The process of collecting, listing, comparing and rejecting data outlined by BACON was too involved for practical application. His error consisted in laying too great stress upon the mere collection and compilation of observations and not enough upon judgment in selecting experiments and in interpreting data. Nevertheless BACON's writings had a wonderful influence in stimulating scientific inquiry and his picture in the *New Atlantis* of the benefits to be derived from coöperative research was the inspiration that led afterwards to the establishment of the Royal Society and various academies of science. His books are remarkably free from the gross medieval superstitions that fill the pages of PARACELSUS and to proceed from the latter to BACON is like ascending from a fog to a higher clearer atmosphere.

BACON applied his method to the study of several problems of present day interest in agricultural chemistry and conducted experiments on germination, composting, maturing of fruits and other natural processes of which several examples are quoted from his "*Sylva Sylvarum*" (10th ed., 1677):—

"Experiments in Consort touching the Acceleration of Germination"

"There was Wheat steeped in Water mixed with Cow-dung. Other in Water mixed with Horse-dung, other in Water mixed with Pigeon-dung, other in Urine of Man, other in Water mixed with Chalk powdered, other in Water mixed with Soot, other in Water mixed with Ashes, other in Water mixed with Bay-salt, other in Claret Wine, other in Malmsey, other in Spirit of Wine. The proportion of the mixture was, a fourth part of the ingredients to the Water, save that there was not of the Salt above an eighth part. The Urine, and Wines, and Spirit of Wine, were simple without mixture of Water; the time of steeping was twelve hours; the time of the year October. There was also other Wheat sown unsteeped, but watered twice a

day with warm Water; there was also other Wheat sown simple, to compare it with the rest. The event was, that those that were in the mixture of Dung, and Urine, Soot, Chalk, Ashes, and Salt, came up within six days; and those that afterwards proved the highest, thickest, and more lusty, were first the Urine, and then the Dung; next the Chalk, next the Soot, next the Ashes, next the Salt, next the Wheat simple of itself unsteeped and unwatered, next the watered twice a day with warm Water, next the Claret Wine. So that these three last were slower than the ordinary Wheat of itself; and this Culture did rather retard than advance. As for those that were steeped in Malmsey, and Spirit of Wine, they came not up at all. This is a rich Experiment for profit; for the most of the steepings are cheap things, and the goodness of the crop is a great matter of gain" (*loc. cit.*, pp. 89-90).

This experiment was well planned in that a control test with "wheat simple" was introduced as a standard of comparison. BACON seems to have been among the first to introduce necessary precautionary checks in making growth experiments upon crops.

"Experiments in Consort touching all Manner of Composts and Help of Ground: —

"The first and most ordinary help is Stercoration. The Sheeps-dung is one of the best; and next, the Dung of Kine; and thirdly, that of Horses; which is held to be somewhat too hot, unless it be mingled; that of Pigeons for a Garden, or a small quantity of Ground, excelleth. The ordering of Dung is, if the Ground be Arable, to spread it immediately before the Plowing and Sowing, and so to Plough it in: For if you spread it long before, the Sun will draw out much of the fatness of the Dung: If the Ground be Grazing Ground, to spread it somewhat late towards Winter, that the Sun may have the less power to dry it up. As for special Composts for Gardens (as a Hot Bed &c.) we have handled them before.

"The second kind of Compost is the spreading of divers kinds of Earth as Marl, Chalk, Seasand, Earth upon Earth, Pond-Earth, and the mixtures of them. Marl is thought to be the best, as having most fatness. And not heating the Ground too much. The next is Sea-sand, which (no doubt) obtained a special vertue by the Salt; for Salt is the first rudiment of life. Chalk over-heateth the Ground a little; and therefore is best upon cold Clay-Grounds, or Moist-Grounds: But I heard a great Husband say, that it was a common error to think that Chalk helpeth Arable Grounds, but helpeth not Grazing Grounds, whereas (indeed) it helpeth Grass as well as Corn. But that which breedeth the error is, because after the chalking of the Ground, they wear it out with many Crops without rest; and then (indeed) afterwards it will bear little Grass; because the Ground is tired out. It were good to try the laying of Chalk upon Arable Grounds, a little while before Ploughing, and to Plough it in, as they do the Dung; but then it must be Friable first, by Rain or Lying: As for Earth it Compasseth itself; for I knew a great Garden, that had a Field (in a manner) poured upon it, and it did bear Fruit excellently the first year of the Planting; for the Surface of the Earth is ever then fruitfulest: And Earth so prepared hath a double Surface. But it is true, as I conceive, that such Earth as hath Salt-Peter bred in it, if you can procure it without too much charge, doth excel. The way to hasten the breeding of Salt-Peter, is to forbid the Sun, and the growth of Vegetables. And therefore, if you make a large Hovel, thatched over some quantity of Ground; nay, if you do but plank the Ground over, it will breed Salt-Peter. As for Pond-Earth or River-Earth it is a very good compost, especially, if the Pond have been long uncleansed, and so the Water be not not too hungry; and I judge it will be yet better, if there be some mixture of Chalk.

"The third help of Ground is, by some other Substances that have a vertue to make Ground Fertile, though they be not meerly Earth, wherein Ashes excel; inso-much as the countries about Etna and Vesuvius have a kind of amends made them, for the mischief the eruptions (many times) do, by the exceeding fruitfulness of the soyl, caused by the Ashes scattered about. Soot also, though thin, spread in a Field or Garden, is tried to be a very good compost. For Salt it is too costly; but it is tried, that mingled with Seed-corn, and sown together, it doth good: And I am of opinion, that Chalk in Powder, mingled with Seed corn, would do good: perhaps as much as Chalking the Ground all over. As for the steeping of the Seeds in several

mixtures with Water, to give them vigor, or watering Grounds with Compost-water, we have spoken of them before.

"The fourth help of Ground is, the suffering of Vegetables to die into the Ground, and so to fatten it; as the Stubble of Corn, especially Pease. Brakes cast upon the Ground in the beginning of Winter, will make it very fruitful. It were good (also) to try whether Leaves of Trees swept together with some Chalk and Dung mixed, to give them more heart, would not make a good Compost: For there is nothing lost, so much as Leaves of Trees, and as they lie scattered, and without mixture, they rather make the Ground sowre, than otherwise" (*loc. cit.*, pp. 122-3).

This extract is not so much a plan of experiments as a review of old agricultural practices. The reference to marl as "having most fatness" will remind the reader of PLINY and PALISSY, although the latter would reject the idea that "chalk overheath the ground". PLINY, as we have seen, regarded the practice of placing "earth upon earth" as a piece of madness. The mention of salt as "the first rudiment of life" is in full accord with the views of PARACELUS and PALISSY and this belief was repeated with even greater emphasis by later writers:—

"Experiment in Consort touching the Maturation of Fruits:—"

"As for the Maturation of Fruit, it is wrought by the calling forth of the Spirits of the Body outward, and so spreading them more smoothly, and likewise by digesting, in some degree, the grosser parts: And this is effected by Heat, Motion, Attraction, and by a Rudiment of Putrefaction: For the Inception of Putrefaction hath in it a Maturation.

"There were taken Apples and laid in Straw, in Hay, in Flower, in Chalk, in Lime, covered over with Onions, covered over with Crabs, closed up in Wax, shut in a Box, &c. There was also an Apple hanged up in smoak. Of all which the Experiments sorted in this manner.

"After a months space, the Apple, enclosed in Wax, was as Green and fresh as at the first putting in, and the Kernels continued White. The cause is, for that all exclusion of open Air, (which is ever predatory) maintaineth the Body in his first freshness and moisture; but the inconvenience is, that it tasteth a little of the Wax, which, I suppose, in a Pomegranate, or some such thick coated fruit, it would not do.

"The Apple hanged in the smoak, turned like an old Mellow-Apple wrinkled, dry, soft, sweet yellow within. The cause is, for that such a degree of heat, which doth neither melt nor scorch (for we see that in a greater heat, a roast Apple softneth and melteth, and Pigs feet made of quarters of Wardens, scorch and have a skin of coal) doth Mellow, and not adure: The smoak also maketh the Apple (as it were) sprinkled with Soot, which helpeth to Mature. We see that in drying of Pears and Prunes, in the Oven, and removing of them often as they begin to sweat, there is a like operation: but that is with a far more intense degree of heat.

"The Apples covered in the Lime and Ashes were well matured as appeared both in their yellowness and sweetness. The cause is, for that Degree of Heat, which is in Lime and Ashes, (being a smothering heat) is of all the rest most proper; for it doth neither Liquefie nor Arefie, and that is true Maturation. Note, that the taste of those Apples was good, and therefore it is the Experiment fittest for use.

"The Apples covered with Crabs and Onions, were likewise well Matured. The cause is not any heat, but for that the Crabs and the Onions draw fourth the Spirits of the Apple, and spread them equally thorowout the Body; which taketh away hardness. So we see one Apple ripeneth against another: And therefore in making of Cider, they turn the Apples first upon a heap; so one Cluster of Grapes that toucheth another whilst it groweth, ripeneth faster. *Botrus contra Botrum citius maturescit.*

"The Apples in Hay and Straw, ripened apparently, though not so much as the other, but the Apple in the Straw more. The cause is, for that the Hay and Straw have a very low degree of Heat, but yet close and smothering, and which dryeth not.

"The Apple in the close Box was ripened also. The cause is, for that all Air kept close, hath a degree of warmth; as we see in Wool, Fur, Plush, &c.

"Note, that all these were compared with another Apple of the same kind that lay of it self; and in comparison of that, were more sweet, and more yellow, and so appeared to be more ripe.

"Take an Apple, or Pear, or otherlike Fruit, and Roul it upon a Table hard: We see in common experience, that the Rouling doth soften and sweeten the Fruit presently, which is nothing but the smooth distribution of the Spirits into the parts; for the unequal distribution of the Spirits maketh the harrishness: But this hard Rouling is between Concoction and a simple Maturation; therefore, if you whould Roul them but gently perhaps twice a day, and continue it some seven days, it is like they would Mature more finely, and like unto the Natural Maturation.

"Take an Apple, and cut out a piece of the top, and cover it, to see whether that Solution of Continuity will not hasten a Maturation. We see that where a Wasp, or a Fly, or a Worm, hath bitten in a Grape, or any Fruit it will sweeten hastily.

"Take an Apple &c. and prick it with a Pin full of Holes, not deep, and smear it a little with Sack, or Cinnamon Water, or Spirit of Wine, every day for ten days, to see if the Virtual Heat of the Wine or Strong-Waters, will not Mature it.

"In these Tryals also, as was used in the first, set another of the same Fruit by, to compare them, and try them by their Yellowness, and by their Sweetness" (*loc. cit.*, pp. 70-1).

This passage illustrates BACON's "dragnet" practice of including in his investigations every conceivable kind of test such as covering apples with crabs. The maturation experiments with their control by comparison trials were well planned although BACON showed an over-readiness to explain some of his observations upon the basis of preconceived ideas such as that of crabs and onions drawing "fourth the spirits of the apple". His experiments are weakest because of their failure to consider quantitative relations. But taken all in all BACON's work, as it relates to agricultural chemical research, was an immense advance over anything that had preceded it. It marked the beginning of a new era in the art of experimentation.

It is seen from the passages quoted that BACON was most industrious in accumulating observations and the modern student can find many hints in his writings for worthy investigations. His observation, for example, about one fruit hastening the ripening of another is most suggestive. It had been observed many times but science had to wait over three centuries after BACON's death before this puzzle could be solved by the aid of delicate chemical methods for detecting traces of ethylene.

BACON's countless observations, with all the help of his new logic machine, did not lead him to the establishment of a single general law. He should not be blamed, however, for the faulty explanations which he gave for many of his observations, as these simply reflect the undeveloped state of knowledge in his time. It must be remembered, moreover, that BACON viewed the world of nature as a whole and not from the standpoint of any particular science. He looked with disfavor upon specialization and this no doubt explains his antipathy to chemists, of whom he had PARACELSUS in mind as the chief representative, when he said: —

"by wandering through the wilds of experience they sometimes stumble upon certain useful discoveries; not by reason, but by accident; whence proceeding to form theories, they plainly carry the smock and tarnish of their art along with them. . . . These childish operators at the furnace must needs be raising philosophy from a few experiments of distillation; and introducing, at every turn, their own idols of separation and analysis, where no traces of them are really found" (Works, 1818, Vol. XI, pp. 271-2).

BACON's political downfall in 1621 led to his retirement from public life and to devoting his five remaining years to the production of several works in literature, philosophy and science that in their value to the world have far outweighed all that he accomplished as a statesman. His zeal for science continued to the very end. An experiment, which he was conducting on the preservation of a dressed fowl by means of snow, led to the contraction of a chill, from the effects of which he died on April 9, 1626.

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Angelo Sala (1575-1640):— One of the most advanced thinkers among the chemists of the late sixteenth and early seventeenth centuries was ANGELO SALA. He was born in Vicenza, Italy, but moving northward at an early age spent the remainder of his days in Germany and Switzerland. He studied medicine and after practicing in Dresden and other cities became physician to the Duke of Mecklenburg in whose service he died. SALA was a man of independent practical judgment and remarkably free from the superstitions of the Paracelsian and Galenical schools between whose extremes he steered a median rational course. He ridiculed the idea of the philosopher's stone, or of a universal elixir, and avoiding all pretentious theorizing confined his attention to fact and observation.

SALA's writings, in addition to the discussion of medical subjects, contain several treatises relating to chemistry and technology. His "Saccharologia" discusses the manufacture, refining and utilization of sugar; his "Tartarologia" the preparation and properties of various tartars or salts of vegetable acids; and his "Hydraeleologia" the distillation of volatile essences and alcoholic spirits. These works belong to the beginnings of agricultural-chemical technology. The following abstracts and translations are taken from the "Saccharologia" (Rostock 1637).

SALA states that thousands of people gain their living from the production of sugar from sugar cane and that the trade in sugar is as important as that in oil, salt, wine, wool, and spices. The raw sugar, obtained by purifying and concentrating the expressed juice of the cane, is shipped in the crude state to Europe where the sugar refiners remelt and convert it into purer products. The numerous grades of sugar include the various types of raw and refined products. Of the latter six kinds are preferred—snow-white shining crystals, common white crystal sugar, yellowish "farine", yellow but pure sweet "farine", reddish "farine" of varied flavor, and white hard dry loaf sugar. In the preparation of these sugars various sirups are obtained as by-products. A low-grade thick brownish-colored molasses (Melazzo) of a sweet empyreumatic flavor is used by the poor as a sweeten-

ing agent in place of honey and also by bakers who prefer it for making cakes partly because of its lower cost and partly because of the fine brown color which it gives their wares. A higher, bright yellow grade of sirup

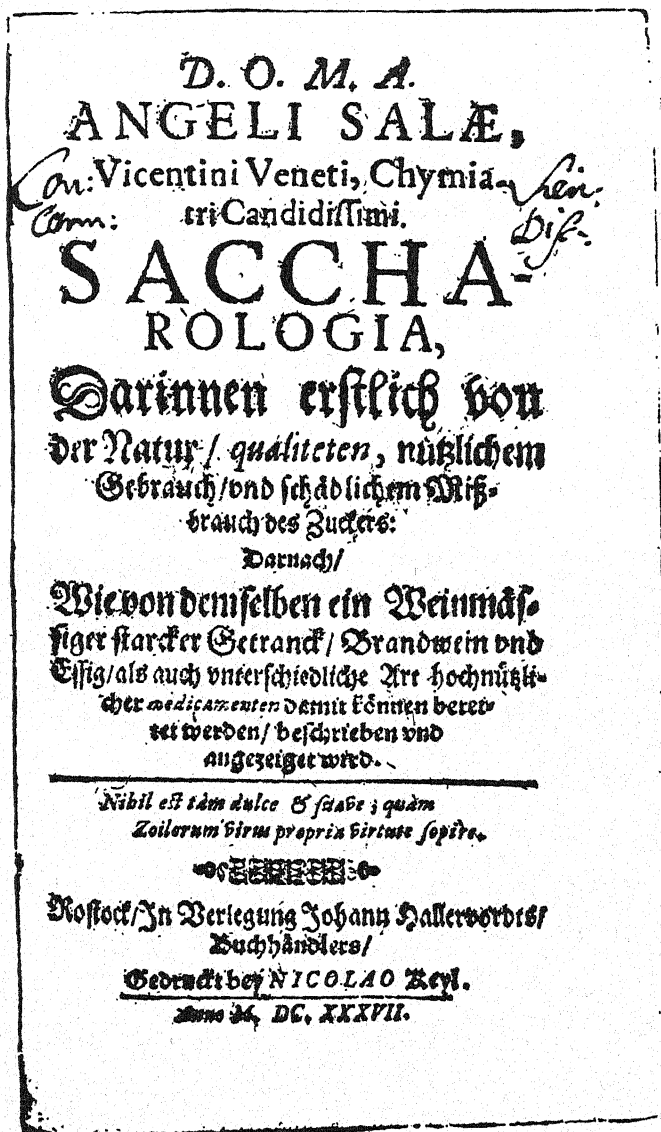


FIG. 11. — Title page of the "Saccharologia" of ANGELO SALA.
 Rostock, 1637.

has the sweetness of honey and is especially suited for preserving fruits. The highest grade of sirup is a pure white concentrated solution of sugar itself. SALA thus describes the refining of sugar : —

"What especially relates to the refining (refinement) of sugar, this is the art by which the above-mentioned sugars after their first extraction are further purified, made whiter, brighter, and drier and given a much more beautiful outward appearance than they had before. This art involves different operations such as dissolving; boiling; skimming; clarifying; evaporating the sugar to its proper consistence; pouring into moulds; draining off and separating the adhering sirup, or the dark dirty fatty sticky substance, from the hardest part; removing it from the moulds at the right time; drying it; and bringing it to the proper grade of excellence, such as fine, superfine, extra fine, candy, etc., according to the taste of the refiner.

"The best agent of all which the refiner can employ for this work is well-settled crystal-clear lime-water or lye, in which one part of lime is slacked. In this lye the unrefined sugar is dissolved (after having been first clarified with egg white to remove dirt, sand, etc., and then moulded into great loaves), boiled, skimmed and then poured into moulds of another kind in which the above-mentioned dark thick syrup or melazzo drains off and drips through a hole at the bottom into special receptacles. This operation is repeated several times (more or less according as the raw sugar was white, yellow or brown and according to the desired grade of the finished product) until the intended result is obtained. The lime water, owing to its sharp caustic qualities, extracts the dark syrupy impurities from the sugar and leaves behind only the whitest and hardest part which is like salt. Which process is to be regarded, not unjustly, as a beautiful invention."

After disproving that the lime water used as a clarifying agent imparts any undesirable flavor to the refined sugar, SALA discusses the various uses of sugar for dulcifying medicines; for making marmalades and other preserves of quinces, peaches, etc.; for making marchpane, sugar bread and other bakery products; for making cordials, liqueurs, and essences, from flowers, herbs, roots, spices, etc.; and for making fermentation products as wine, beer, brandy, and vinegar.

In so far as existing knowledge and art permitted SALA attempted to determine the "elementary substantial composition" of sugar and found it to consist, the same as other vegetable products, of water, oil, salt and earth. He then describes the "spagyric" experiment by which he arrived at this result:—

"Put two pounds of the desired kind of sugar in a strong, capacious, high glass flask (because sugar on heating froths up strongly), place it on a sand bath, connect with a wide helm, provide a recipient, seal up connections in the customary way and then heat gently at first until water begins to distil over. Continue the process without heating too strongly, as this might cause breakage of the apparatus. When the distillation slackens to a slow dropping and the sugar ceases to foam up so strongly as at first, increase the heat until no more moisture, steam or smoke is evolved. After cooling and opening the apparatus, the water of the sugar will be found in the recipient and swimming upon its surface a brownish oil, varying in quantity according to the amount of sugar taken. Unrefined sugar gives more oil than refined. The burned residue of sugar in the flask is detached and incinerated in a crucible or earthen dish to an ash. The oil is separated from the water (in the manner described for such products in my *Hydraeleologia* and as known to every distiller) and preserved in a special bottle. The water can be rectified and made clear by distilling on a sand bath. The ash is finally extracted with distilled water, the clear lye decanted, evaporated and coagulated to a salt according to the methods described for salts in my *Tartarologia* and which are familiar to every chemist. The insoluble part from which the salt was extracted is a fine tasteless earth of no special noticeable qualities. The four substances thus isolated from the sugar are each placed in a separate receptacle."

The extracts quoted, with their concise descriptions and total absence of mysticism, might seem to have been taken from a modern chemical or technological treatise.

In other branches of chemistry SALA was also a leader in advance of his time. He emphasized the fact that the ash, oil, etc., which were obtained by destructive distillation, existed in different forms in the original plant material. He was the first to synthesize sal ammoniac by neutralizing volatile salt from urine (ammonium carbonate) with spirit of salt (hydrochloric acid). He announced that spirit of vitriol (sulfuric acid) could be produced by burning sulfur in a moist atmosphere in which process something was taken from the surrounding air (*ab ambiente aere extractum*) — an explanation which anticipated the later one of LAVOISIER and was directly contrary to the phlogistic interpretation of STAHL. SALA defined fermentation as “an intimate movement of elementary particles which tend to group themselves in a different order with the production of a new compound”, a definition which was better than most of the ones proposed during the next two centuries. Had SALA only employed quantitative methods to sustain his experiments his sagacious mind would no doubt have solved many of the problems that perplexed chemists for the next two centuries.

REFERENCE:—

SALA, ANGELO (1637): *Saccharologia*, darinnen erstlich von der Natur, qualiteten, nützlichem Gebrauch und Schädlichem Missbrauch des Zuckers. Darnach wie von demselben ein Weinmässiger starcker Getranck, Brandwein und Essig, als auch unterschiedliche Art hochnützlicher Medicamenten damit können bereitet werden, beschrieben und angezeigt wird. Rostock.

Jan Baptista van Helmont (1577-1644):— J. B. VAN HELMONT, a Belgian physician, iatrochemist and a younger contemporary of BACON, was the first to initiate quantitative chemical experiments in the study of plant life. Although he inaugurated thereby a new era in agricultural science, he was greatly hampered in the drawing of correct conclusions from his experiments by ideas inherited from PARACELSUS and from the old Greek philosophy. Like PARACELSUS he ridiculed the scholastic philosophers for their stupidity and failure to be convinced by experimental proofs. He accepted the three principles of PARACELSUS but modified the doctrine of the four elements by reviving the ancient theory of THALES that water was the primary substance from which the world of matter was derived. As proof of this he claimed to have completely reduced stones, sulfur, metals, honey, wax, oils, bone, brain, cartilage, wood, bark, and leaves to the state of tasteless water.

VAN HELMONT was born at Brussels, the son of a nobleman of Brabant. He was educated at Louvain, where, after pursuing the study of one science after another, he finally took up medicine in which subject he became a disciple of PARACELSUS, whom he greatly surpassed, however, in knowledge and civility. He took his degree of Doctor of Medicine in 1599 and after a period of travel settled finally on his estate at Vilvorde, near Brussels. Here, in the intervals of his medical practice, he occupied himself with chemical experiments until his death on December 30, 1644. His manuscripts were collected, edited and published by his son FRANZ MERCURIUS VAN HELMONT at Amsterdam in 1652 under the title “*Ortus Medicinæ*”. It is from passages in this work that the following translations are made.

Although endowed with scientific ability far beyond that of PARACELSUS, VAN HELMONT shared the latter's inclination towards magic and the super-

natural. He believed in the Archeus, the inner regulator of digestion, whom he called the guardian of life and the promoter of transmutations (*Vitæ custos et transmutationum promotor*). Yet while retaining this mystical conception of PARACELSUS he had clear ideas about the acidity of the gastric juice, the alkaline nature of the bile, and the digestive action of other secretions. In this respect he far excelled PARACELSUS. VAN HELMONT in fact deserves the credit of having taken the first steps in the science of physiological chemistry.

Seminalis enim concreti proprietas, quæ in Gas perfeverat, vi frigoris, & dierum maturitate
monitur, & in pristinam aquam Gas redit. O- 30
mnia verò vegetabilia immediate, & materialiter,
ex solo aquæ elemento prodire hac mechanica didici.
Capi enim vas terreum, in quo posui terræ in
clibano arefactæ lb 200, quam madefeci aqua pluvia,
illique implantavi truncum salicis, ponderantem lb 5. ac tandem exacto
quinquennio, arbor inde prognata, pendebat 169 lb,
& circiter uncias tres. Vas autem terreum, sola aqua pluvia,
vel distillata, semper (ubi opus erat) maduit,
eratque amplum, & terræ implanatum, & ne pulvis obvolitans
terræ commisceretur, lamina ferrea, stanno obducta,
multoque foramine pervia, labrum vasis tegebatur.
Non computavi pondus foliorum quatermo autumnis deciduorum.
Tandem iterum ficcavi terram vasis, & repertæ sunt eadem
libræ 200 duabus circiter unciis minus. Libræ ergo 164
ligni, corticum, & radicum, ex sola aqua surrexerant.
Carbo ergo, cum totus fit 31
ex aqua, si reducatur in fonte aliquo in lapidem;
non poterit per aquam commutari in lapidem,
nisi etiam totus iste lapis sit materialiter mera aqua.
Pisces enim ut ex aquis mult- 32
tam axungiam faciunt: ita vicissim omnis pinguedo

FIG. 12.— *Specimen of Latin text of van Helmont's "Ortus Medicinæ", Amsterdam, 1652, p. 88.*—In the second and third lines occurs the word "Gas" which VAN HELMONT first coined in this volume. In lines 6 to 22 VAN HELMONT describes his famous plant growth experiment with a willow tree—the earliest recorded experiment of the kind.

As an example of VAN HELMONT's method of experimenting, the following passage is quoted from his "Ortus Medicinæ". It is interesting as marking the first appearance of the word "gas" in chemical literature:—

"From 62 pounds of oak charcoal there is obtained by combustion one pound of ash. The remaining 61 pounds therefore consist of that spirit of wood (*spiritus sylvester*) which even under ignition can not escape from a closed vessel. This spirit, hitherto unknown, I call by the new name Gas. . . . Many bodies in fact contain this spirit and certain ones are entirely converted into it, not indeed because it is actually present in them as gas (since it could not be held in a compact form but would entirely escape) but it exists there as a condensed spirit, fixed like a corporeal substance from which it may be liberated by the action of a ferment, as in the case of wine, must, bread, mead, and the like" (*loc. cit.*, p. 86).

VAN HELMONT'S *spiritus sylvestre*, or *gas sylvestre*, is of course the fixed air or carbon dioxide of later investigators. His identification of the gas produced by the burning of wood charcoal with that obtained in fermentation is one of the first important generalizations in the history of agricultural chemistry. He erred in supposing this gas to be a transformation product of water, but VAN HELMONT always gave a reason for the truth as he saw it and it is interesting to trace the lines of his argument in a famous experiment which has been quoted by many writers from BOYLE to the present time:—

"I was able to show by the following experiment that all vegetables are produced immediately and materially from the single element water. I took an earthen vessel in which I placed 200 pounds of soil previously dried in an oven. I then watered it with rain water and planted therein a willow branch weighing 5 pounds. After an interval of 5 years the tree which had sprung up weighed 169 pounds and some 3 ounces. The earthen vessel which was always watered when necessary with rain or distilled water was large and embedded in the ground; lest any flying dust should get mixed with the soil an iron cover plated with tin and provided with a large opening closed the mouth of the vessel. I did not determine the weight of leaves which fell during the four months. At the end of the experiment I dried the soil again in the vessel and obtained the same weight of 200 pounds lacking about 2 ounces. The 164 pounds of wood, bark and roots were therefore derived from water alone" (*loc. cit.*, p. 88).

As Sir MICHAEL FOSTER has observed, this research is one of which an agricultural experiment station of today need not be ashamed. Although the conclusion is entirely wrong, the technique is excellent. It is a striking fact that, when a century and a half later the true source of the cellular substance of plants was determined, the carbonaceous matter of the wood, bark and roots of VAN HELMONT'S tree was proved to have its origin not in water but in the *gas sylvestre* which he himself had discovered.

REFERENCES:—

- FOSTER, Sir M. (1901): Lectures on the History of Physiology during the sixteenth, seventeenth and eighteenth centuries. Cambridge, University Press, p. 133.
HELMONT, J. B. VAN (1652): *Ortus Medicinæ. Id est, Initia Physicæ inaudita. Progressus Medicinæ novus, in Morborum Ultionem, ad Vitam longam.* Amsterodami, apud Ludovicum Elzevirium.

Johann Rudolph Glauber (1604–68):—Another famous member of the iatro-chemical school, who contributed to the advancement of agricultural chemistry, was the German chemist, J. R. GLAUBER. He was born at Karlstadt in Franconia and after wandering from place to place in Germany during the troubled period of the Thirty Years War went finally in 1648 to Amsterdam where he spent much of the remainder of his life and where most of his works were published.

GLAUBER'S first book was his *Furni Novi Philosophici*, or to translate part of the full title, "New Philosophical Furnaces or a description of the New Art of Distilling; especially adapted to the preparation of spirits, oils, flowers and other medicinal products, by a very easy peculiar way from plants, animals and minerals," which was published in five parts at Amsterdam in 1648. In this very practical work, which deals with the construction and operation of furnaces, distilling apparatus and other technical equipment, occurs much of agricultural chemical interest. The preparation of essential oils from spices, seeds, flowers and other plant products, the

making of pyroligneous acid by the destructive distillation of wood and the malting of grain for the manufacture of distilled spirits are all described with illustrations of apparatus.

GLAUBER was the author of over twenty different publications which were translated into English by CHRISTOPHER PACKE, the entire collection being published at London in 1689 in a large folio volume under the title "The Works of the highly experienced and famous Chymist JOHN RUDOLPH GLAUBER: containing Great Variety of Choice Secrets in Medicine and Alchemy, in the Working of Metallick Mines, and the Separation of Metals. Also, various Cheap and Easy Ways of making Saltpetre, and Improving of Barren-Land, and the Fruits of the Earth." It is to the second edition of this work, published in 1694, that the citations of this sketch refer.

GLAUBER was an ardent follower and expounder of PARACELSUS, whom he resembled so much in manners, superstitions and wandering mode of life, that he has been called the PARACELSUS of the seventeenth century. He expressed his contempt for higher learning and boasted that his books were based upon first hand knowledge derived from experience.

"I confess ingeniously", he writes, "that I never frequented the Universities, nor ever had a mind so to do; for should I have so done, haply I should never have arrived to that knowledge of Nature, which I mention without boasting, as I now possess; neither doth it ever repent me, that I have put my hands to the Coals, and have by the help of them penetrated into the knowledge of the Secrets of Nature" (*loc. cit.*, Part I, p. 307).

Like the books of PARACELSUS and VAN HELMONT, the works of GLAUBER are deeply tinged with superstition and mysticism. He made the three principles of salt, sulfur, and mercury the basis of his philosophy but laid chiefest stress upon salts. He held that PARACELSUS had this in mind, when he foretold the coming of a chemical messiah, whose name, ELIAS, GLAUBER supposed to be a secret anagram of Selia (*i.e.*, Salia) meaning salts (*loc. cit.*, Part 3, p. 52). One of these salts, the *sal mirabile* (sodium sulfate), which he discovered, now bears the name of "Glauber's salt". But the greatest of salts according to GLAUBER is Sal Petrae or nitre. The following passage gives a glimpse of his chemical philosophy and style:—

"Sal nitre is the only growth, generation and encrease of all Vegetables, Animals and Minerals, as also their Destruction and Regeneration, by a perpetual Circulation of the Elements, by which things being dissolved, do again return into the same from which they arose; For the Nitre of Vegetables in the bodies of Animals, by the intervening digestions and separations, is generated into a Mineral Salt, which none will deny; and Nitre, or Salt of the Earth, is Vegetable, Mineral, and Animal, which cannot be said of any other subject but the Universal Matter. And even as it is the chief Conservator of Vegetables, Animals and Minerals, so it is also their Destroyer and Death; therefore by them it is both loved and hated. Vegetables love it, when growing in the Earth, they thence draw their nourishment; for when the Earth is dead, or void of Salt, it affordeth neither nourishment or increase to seed, Christ himself being witness, when he saith, 'Ye are the Salt of the Earth': but if the Earth be destitute of Salt (or the Salt hath lost his saltness) it is altogether dead, and can bring forth no fruit. An ignorant man saith, that Dung maketh the Earth fruitful, but undeservedly, for not the Dung, but the Salt which lies hid in the Dung, doth this, which is generated of Vegetables after their putrefaction, and again transmuted into their seeds and roots which are in the Earth; the same Animals again receive in their food, whereby their bodies are strengthened and preserved from Corruption. For no man is so rude, but

he hath learned by experience, that Salt is the Preserver of things both living and dead. But an ignorant man may object, that other things also have a preservative power, as myrrh, aloes, and other Balsamick Liquors, which preserve Flesh and Fish from putrefaction. To this I answer, That it is not myrrh or aloes, but their salt which effecteth this. Honey also and sugar preserve things, which are not salts. I answer, That Thou understandest not the nature of Salts; those are sweet salts, the other are bitter salts, which by putrefaction are changed into sowre and acid. Also every burning spirit of Wine, and other Vegetables, preserveth other bodies although they are not in form of salt, nevertheless it is nothing else but the most pure volatile salt of the Wine; mixed with its sulphur, which doth this; for none of the Principles is sincere, and wholly free from the mixture of the rest" (*loc. cit.*, Part I, pp. 168-9).

This passage, like one cited from PARACELSUS, expresses an imperfect realization of a continual circulation of elements between the mineral,



- A. Fornax cum globo cupreo.
- B. Globus cupreus.
- C. Vas destillatorium.
- D. Vas refrigeratorium cum serpente.
- E. Excipulum sive vas recipiens.
- F. Sedilia, quibus vasa insident.

FIG. 13. — *Glauber's Apparatus for the Steam-Distillation of Plant Materials.* — A, Furnace. B, Copper Vessel in which water is boiled. C, Barrel containing the plant materials which are subjected to the action of the steam from B. D, Barrel of cold water with coils for condensing the distillate from C. E, Recipient for the condensed distillate from D. F, Stools for supporting the barrels. Illustration from GLAUBER'S "Furni Novi Philosophici", 1648.

vegetable and animal kingdoms, but it was much too early for a clear expression of the details of this important relationship. GLAUBER held the same views as PALISSY regarding the nature of salts and their function as the essential part of animal manure.

GLAUBER was a sincere patriot and, when he saw Germany ruined as a result of the long Thirty Years War, wrote his famous Prosperity of Germany (*Deutschlands Wohlfarth*) in which he admonished his countrymen to avoid the wastage of the nation's natural resources. It was the same sort of advice given earlier by PALISSY in his "Récepte Véritable" to the people of France. Grain must not be allowed to deteriorate, food and wine must not be permitted to spoil and the raw materials of the country must be better utilized so that Germany might produce at home what she could not afford to purchase abroad. It was a situation destined to have an almost exact parallel in Europe three centuries later after the first World War. The principles of self-sufficiency and of salvation by the aid of chemistry, which GLAUBER preached, are similar to those proclaimed today.

The conditions during the Thirty Years War, when predatory armies with their camp followers plundered the peasantry, and after devouring one part of the country moved on to the next, have been described by GLAUBER in numerous passages:—

"Consider," he writes, "when the Souldiers have taken away the Horses and Carts, carried away the Oxen, devoured the Cows and Sheep, and wasted the whole Country, by what means shall the wasted Fields be dunged and restored to the Husband-man, that returning to their former fruitfulness, he may reap from them the expected Fruit" (*loc. cit.*, Part I, p. 193).

In this situation, when there were no cattle to supply the manure which was the primary need for restoring fertility to devastated fields, GLAUBER invented as a substitute his "Philosophic Dung", or "Fattening Salt". He thus describes its composition:—

"Of this salt, which we may use instead of dung, there is great diversity, for it is prepared of Wood-ashes, of Stones burnt to Lime, and of other bodies putrefied by length of time. But the Chief of all these is Salt-petre, being the salt of Vegetables, Animals and Minerals putrefied, especially because it is endowed with a certain occult and sweet Fire. Also the signature proper to it, clearly exposeth to our sight its augmentative virtue; for it exhibits not itself in a cubical form, as is observed in corrosive salts, (altogether adverse to the augmentation of Bodies) but Dart-like or acuminate" (*loc. cit.*, Part I, p. 224).

GLAUBER's "Fattening Salt," with its content of lime, potash, phosphoric acid and nitrogen, might be called the first complete mineral fertilizer. The inference of the augmentative virtue of saltpeter from its crystalline form is an application of the Paracelsian doctrine of signatures, in accordance with which the beneficial or injurious action of a substance could be deduced from its physical appearance. This peculiar belief persisted even until modern times. GLAUBER's insistence upon the fertilizing value of saltpeter is repeated again and again, as in the following passage:—

"In the first place, and above all, this is here to be considered as a main principle, (*viz.*) that all those things which dung the Fields and Lands, and fatten them, must necessarily contain in them Salt-petre. For from this only, and alone, comes all the fertility throughout the whole Earth, which Axiome cannot be gainsayed" (*loc. cit.*, Part I, p. 309).

GLAUBER, following BIRINGUCCIO and AGRICOLA, gives full directions for manufacturing this highly important salt from the dung of animals,

urine, waste vegetable matter, and other refuse by allowing the materials to nitrify in beds, leaching with a lixivium of wood ashes and then evaporating the effluent from the beds to the point of crystallization. In this way was obtained the salt which GLAUBER considered so essential not only to supply the needs of agriculture but to make the gunpowder necessary for the national defense. The macerating of seeds in a solution of saltpeter was recommended by GLAUBER to promote germination. GLAUBER's process for making saltpeter was introduced into New England in the middle seventeenth century by the younger WINTHROP.

As to the origin of the saltpeter produced in this way GLAUBER believed it to have been an intrinsic part of the grass and other herbage that was eaten by farm animals, for the same fertilizing action obtained with dung, is secured by the composting of vegetable matter alone.

"I demand," he writes, "whence the common Nitre is gotten? Is it not out of the Earth, which is digg'd out of the Stables where Beasts stand? For it has insinuated it self into (or joined itself with) this (Earth) passing out of the Excrements of the Beasts in length of time, and hath coagulated it self therein, out of which it is at length drawn by pouring on of water, and then is boiled into Salt-petre. Who can deny this? I think no body can. So then if this be granted, that Nitre is found in the Stables where Cattle stand, the Question is, By what means, and way it came into the Stables? It is by the help of the Urine and Excrements which the Beasts have there cast forth. Then again, I ask whether or no those Beasts have those excrements from their Meat and Drink, or from elsewhere? They cannot arise from water, forasmuch as they drink nothing but Water. So that they must necessarily have their rise from the food they eat, and that consists of the Vegetables, Grass and Herbs. Therefore we affirm that the Salt-petre was of necessity in these Herbs, and Grass, afore the Beasts feeding on them. For if it had not been there, it could never have been made in the Beasts Bodies that which it was not afore. For their Stomachs contribute nothing to this operation, save a bare putrefaction. And besides, the Countrymen do even the same thing, for they gather up Stubble, the Leaves that fall from the trees, the Grass, and such like things, and put a great quantity of them into a pit together, and there leave them so long till by the help of Putrefaction they are all turned into Dung, and therewith do they afterwards Dung their Ground (in such wise) as is wont to be done with the Excrements of Beasts. Therefore, forasmuch as that putrefied Grass and Stubble doth dung the ground and render it fruitful, (as well) as the Excrements of Beasts, it must needs be granted, that they have likewise Salt-petre in them" (*loc. cit.*, Part I, p. 309).

GLAUBER criticized the burning of trees for the sole value of the wood ashes as a fertilizing material, without deriving any benefit from the other by-products that went up in smoke:—

"It is sufficiently known," he writes, "that Animals, and Vegetables rotting, dung the earth, and render it fat; which thing even the Rusticks have now learned, that they do the same without putrefying or rotting, when they cut down, and burn the Trees and Bushes, which had grown up in the Fields, during the long time of the War, and spread the Ashes on the ground, by which it is fatned. But that they know not how to save, invert and use with the Ashes for dunging, the acid Spirit, and hot Oyl, which vanish in the burning, ought to seem strange to none, seeing that no man hath hitherto declared it to them" (*loc. cit.*, Part I, p. 189).

The conversion of waste wood by destructive distillation into charcoal, tar, acid distillate (*i.e.*, pyroligneous acid) and other useful by-products is a subject to which GLAUBER frequently refers. The dark tarry oil was considered by him to have a medicinal value in healing ulcers and other sores, and, when taken internally, in curing diseases of the liver, spleen,

bowels, etc. This oil had also the valuable property of preserving wood from decay. When thickened with suet or rosin, it made an excellent substitute for axle-grease. GLAUBER's method of using the oil to protect fruit trees against the attacks of insects, etc. is still employed.

"If you shall imbibe Hempen-Cords, or such as are made of the Bark of Trees twisted together with Grass, with the said Oil, and then bind them about Fruit-trees, it will hinder the creeping up of Spiders, Ants, or Pismires, Palmer or Canker-Worms and other like Insects, which are wont to damnify Fruit; inasmuch as those Insects plainly abhor such hot Oils. By this means also may Rats and Mice be hindered from creeping up Hovel-posts and devouring the Grain" (*loc. cit.*, Part I, p. 192).

The charcoal obtained by destructive distillation of wood was useful as a fuel and the alkaline ashes from its combustion when added to the acid distillate produced a salt which, on exposure to the air, or on mixture with urine, gave rise on long standing, according to GLAUBER, to a saltpeter-containing mixture of such fertilizing value, that one hogshhead of it was superior to several cartloads of common dung. By use of this so-called "fattening salt" GLAUBER declared, in his customary tone of boastful exaggeration, that

"barren places which would never bring forth any fruit, are rendered fertile and fit to bear fruit; so that no place can be found in the world, how barren soever it be, which by this medium may not be rendered fertile. Moreover, this Art is to be greatly esteemed, because by it ground may be fattened in those places where no Cattel are found, and therefore afford no dung; seeing that hitherto no other than the ordinary way of dunging hath been known. So also in places far remote from the Dwellings of men, to which Dung cannot be carried, this Art may be exercised with great profit; especially when Dung is difficult to be procured, or costs dear, and is not carried to those remote places without charge" (*loc. cit.*, Part I, p. 193).

In his description of methods for utilizing the by-products of the waste wood of farms GLAUBER was an early exponent of what in the present day is called "chemurgy". Other methods proposed by GLAUBER for restoring prosperity to a war-ruined country are interesting early examples of applied agricultural chemistry. Among these may be mentioned his very practical suggestion that fruit juices and the liquid extract of malted grain be manufactured in concentrated form so as to prevent deterioration and to reduce the costs of transportation (*loc. cit.*, Part I, pp. 301-6).

As a substitute for ordinary vinegar as a food condiment and preservative in times of scarcity GLAUBER recommended spirit of salt, which he also was the first to term muriatic acid (from the Latin *muria* meaning brine). He prepared pickles, sauces, salads, etc. by means of muriatic acid (*loc. cit.*, Part I, pp. 378-9) and also employed it in place of rennet for coagulating milk in the manufacture of cheese (*loc. cit.*, Part I, pp. 379-81). It is worthy of mention that VIRTANEN in recent times employs hydrochloric acid in his process for making ensilage.

GLAUBER's works are valuable for the information they give regarding the laboratory equipment and technical operations of his time, yet the hold of PARACELSUS upon him was so strong that in the midst of his descriptions he must interject prayers, invocations, and obscure references to dragons and other mythical creatures. He continually interweaves the fabulous with the practical. The compost heap, in his illustration of a nitre-bed, is surmounted by a cock engaged in hatching a basilisk. Like PARACELSUS

and VAN HELMONT, he was a vitalist and believed in an indwelling spirit, or *anima*, which promoted the growth not only of plants and animals but also of metals (*loc. cit.*, Part I, p. 191).

GLAUBER, like PARACELSUS, was a restless, discontented soul and a wanderer from town to town. The reader, who has the courage to wade through the masses of superstition, absurdity, and braggadocio that fill his pages, will find much to reward his patience. He made and described many new compounds of the metals; he was also apparently the first to explain a case of double decomposition or base exchange. His writings are filled with useful bits of practical advice to bakers, brewers, gardeners, and husbandmen. He exerted a great influence during the century in which he lived and in the period following.

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- GLAUBER, J. R. (1651): — *Furni Novi Philosophici, sive Descriptio Artis destillatoriae novae; nec non Spirituum, Oleorum, Florum, aliorumque Medicamentorum illius beneficio, facilima quadam et peculiari via e vegetabilibus, animalibus, et mineralibus, conficiendorum et quidem magno cum lucro; agens quoque de illorum usu tam chymico quam medico, edita et publicata in gratiam veritatis Studiosorum. Amsterodami, apud Joannem Janssonium.*
- (1694): — *The Works. . . containing Great Variety of Choice Secrets in Medicine and Alchemy in the Working of Metallick Mines, and the Separation of Metals. Also, Various Cheap and Easie Ways of making Saltpetre, and Improving of Barren-Land, and the Fruits of the Earth. Together with many other things very Profitable for all the Lovers of Art and Industry. The Second Edition. Translated into English, and Published for Publick Good, by the Labour, Care, and Charge, of Christopher Packe, Philo-Chymico-Medicus, London. Printed for the Author.*

Gabriel Plattes (about 1600-55):—The philosophic career of Sir FRANCIS BACON was coincident in England with the beginnings of a change from the old manorial, or community, type of agriculture to a system of enclosed farms. This transition with its encouragement of individual initiative resulted in a great improvement in the practices of agriculture. The introduction of new crops, such as turnips, clover, and various grasses, enabled farmers to carry a larger number of cattle through the winter, while at the same time the corresponding increase in farmyard manure added greatly to the productivity of their fields. These agricultural improvements stimulated men to give more thought to the theory and economics of agriculture. Some of the early writers of this period applied their imperfect chemical knowledge to the study of agricultural problems. We would refer especially in this connection to GABRIEL PLATTES.

The best known work of PLATTES is his "Discovery of Infinite Treasure" published at London in 1639. Like PALISSY's "Récepte Véritable" and GLAUBER's "Teutschlands Wohlfahrt" it is a plea for the conservation of the nation's agricultural and mineral resources. Waste is to be avoided and improved practices, based upon experimentation, are to be introduced.

PLATTES urges, as the encouragement of experimentation, the establishment of fairer contracts between landlords and tenants: —

"If this were done, then would the Husbandmen be much stirred up to trie experiments; and if they should but spend their spare times in these workes, there is no question, but that many fat veines of marle, chalke, limestone and other earth, would be discovered in many places which now lie hidden, and doe no good at all" (*loc. cit.*, p. 16).

PLATTES truly observes that crops derive their sustenance from the air and from the soil, but it is from lack of the necessary soil nutriments that they chiefly suffer: —

"All fruits are compounded of a double substance, the one terrestriall and the other aethereall, and for the most part, the want of the terrestriall part causeth ill successe" (*loc. cit.*, pp. 14-15).

The valuable crop-sustaining ingredient of soils is of an unctuous nature and hence termed by PLATTES their "fatnesse". Soils may suffer, however, from an excess, as well as from a deficiency of fatness and in the case of peaty soils the excess of fatness may even render them combustible: —

"There the cure is to cut up a part thereof into turfes, and when they are dried to set them on fire, and so to strow the ashes amongst the rest, to bring it to a temperament.

"For I finde a double fatnesse in every compounded Body, the one combustible, the other incombustible; the combustible fatnesse causeth vegetation by its rarifying and vapping qualitie, when it feeleth the heate of the Sunne; the incombustible or fixed fatnesse causeth coagulation of the said vapours by heate of the sunne likewise by its adstringent qualitie, and of these two fatnesses, are all riches and treasures engendered" (*loc. cit.*, p. 23).

PLATTES adhered to the old conception of hot and cold soils and hot and cold manures, in this respect being less progressive than PALISSY. A hot manure, such as that of poultry, with an excess of combustible fatness, should be applied, according to PLATTES, only to cold soils. A very hot manure, as lime, may be used for tempering a cold manure, as that of cows: —

"There is no difference of dungs, but as the incombustible astrigent fatnesse doth overmatch, or is overmatched by, the combustible; so it is more or lesse apt for the cold, or an hot ground" (*loc. cit.*, p. 27).

"The dung of Sheepe is a very temperate manure for much Corne ground, and is not so hot as Lime, Pigeons dung or Poultry dung; nor on the other side, so cold as Cow dung or Oxe dung and therefore to supply the place of it, there is required a composition of lime and dung together . . ." (*loc. cit.*, p. 34).

The fertility of the land, according to PLATTES, was depleted not only by the removal of crops but also by the erosion of floods.

"The Land floods doe carry away the fatnesse from the arable land, and all high grounds, in huge quantities into the Sea; which is further manifested, by the leaving of some small part thereof in the meadows whereby they are enriched; also the further manifestation of this truth is seene by Nilus in Egypt, the Granarie of the World; where they have no more fertilitie then the water bringeth yearly in his belly in certaine moneths, during its overflowing of the ground" (*loc. cit.*, p. 18).

According to PLATTES the losses incurred by erosion could be more than equalized by diligent applications of his mixed manures. Fertility is

also restored by fallowing, which he explained as the renewal of fatness from condensations brought up from the interior of the earth.

"It is certaine that the new provision of manure by Lime, ashes, Marle, Mussilage, and residence of water, and by the rest of the Inventions, will equalize and overmatch the great quantitie of fatnesse carried yearely into the Sea, if the same shall be industriously put in practice; the subterraneall vapours yearely elevate a great quantitie of fatnesse, though in some places more abundantly than in others; for I have knowne arable land borne good corne time out of minde, with every third yeares rest and fallowing, without any manure at all, but onely by this subterraneall vapour arising from some subterraneall fat substance; but though this be but in some speciall places, yet there is no question but that it helpeth well in all places, though of it selfe it be not sufficient without addition of manure" (*loc. cit.*, p. 81.).

With regard to alchemy, which was the great delusion of his period, PLATTES admitted the possibility of transmutation but urges the alchymists

"to lay aside their Balderdash compositions and illiterate operations I could wish they would totally leave off the practice for their owne good For not one in a thousand of the seekers finde that they seeke; besides that I doe more than three quarters know that the Art is not so lucrous as they doe imagine."

PLATTES, therefore, exhorts all "inventive braines to spend their studie and labour" with him in his new Husbandry. It is pathetic to record that PLATTES, the "discoverer of infinite treasure", was a martyr to science like his predecessor, PALISSY. He could obtain no support for his new reform, and was found dead upon the street, a victim of want and starvation.

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Chapter III

AGRICULTURAL CHEMISTRY IN THE TIME OF THE EARLY ROYAL SOCIETY

Robert Boyle (1627-91): — ROBERT BOYLE, who has been called by some the father of chemistry, was born at Linsmore Castle, Ireland, January 25, 1627, the seventh son and fourteenth child of RICHARD BOYLE, the Earl of Cork. He was a sickly but most precocious boy. At the age of eight he entered Eton College and when only eleven was sent abroad with an elder brother and French tutor to complete his education. After six years of travel and study in France, Switzerland, and Italy he returned home in 1644, after the death of his father, and devoted the remainder of his life to scientific research in collaboration with congenial friends.

BOYLE contributed to the advancement of agricultural chemistry in three ways: first, by demolishing the obstructive doctrines of the four elements and three principles; second, by directing attention to more fruitful concepts of experimental investigations; and third, by encouraging coöperative methods of scientific research.

BOYLE's chemical theories are best set forth in his most famous work, "The Sceptical Chymist", a book in dialogue form, which was published at London in 1661. With regard to the doctrine of three principles, CARNEADES, the sceptic of the dialogue (*i.e.*, BOYLE), admits

"that the divisers and embracers of it have done the commonwealth of learning some service, by helping to destroy that excessive esteem, or rather veneration, where-with the doctrine of the four elements was almost as generally, as undeservedly entertained; yet what has been alledged concerning the usefulness of the *tria prima*, seems to me liable to no contemptible difficulties" (Everyman's Lib. Ed., p. 166).

CARNEADES proves that the doctrine of three principles, when subjected to critical analysis, is open to the same objections as that of the four elements. "How does this hypothesis shew us", he asks, "how much salt, how much sulphur and how much mercury must be taken to make a chick or a pompion" (*loc. cit.*, p. 163). The atomic theory of DEMOCRITUS is suggested as a more fruitful hypothesis than either of the others. What is needed, according to BOYLE, is a clearer concept of the term element and, to clarify the argument, CARNEADES submits the following definition: —

"And, to prevent mistakes, I must advertize you, that I now mean by elements, as those chymists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved" (*loc. cit.*, p. 187).

This is the first clear approach to the present accepted definition of a chemical element. BOYLE believed, however, that elements might be transmuted into one another and from the mistaken observation that plants and fish can grow in water, without addition of nutriment, concluded, as did VAN HELMONT, that water might be regarded as the parent material from which minerals, plants, and animals are derived. He repeated

THE
Sceptical Chymist:

OR
CHYMICO-PHYSICAL
Doubts & Paradoxes

Touching the
EXPERIMENTS

WHEREBY
VULGAR SPAGIRISTS

Are wont to Endeavour to Evince their
SALT, SULPHUR

AND
MERCURY,

TO BE

The True Principles of Things.
To which in this Edition are subjoyn'd divers
Experiments and Notes about the *Produci-
bleness of Chymical Principles.*

Cm OXFORD,
Printed by HENRT HALL for Ric. D^o,
vin, and B. Took at the Ship in St. Pauls
Church-Yard. 1680.

Americana Phil. Soc. 7 May 1897

VAN HELMONT'S willow tree experiment with other plants, as related in the following description:—

"I caused my gardiner (being by urgent occasions hindered from being present myself) to dig out a convenient quantity of good earth, and dry it well in an oven, to weigh it, to put it in an earthen pot almost level with the surface of the ground, and to set in it a selected seed he had before received from me, for that purpose, of squash, which is an Indian kind of pompion, that growes apace; this seed I ordered him to water only with rain or spring water. I did not (when my occasions permitted me to visit it) without delight behold how fast it grew, though unseasonably sown; but the hastning winter hindered it from attaining anything near its due and wonted magnitude; (for I found the same autumn, in my garden, some of those plants, by measure, as big about as my middle) and made me order the having it taken up; which about the middle of October was carefully done by the same gardiner, who a while after sent me this account of it: 'I have weighed the pompion with the stalk and leaves, all which weighed three pound wanting a quarter; then I took the earth, baked it as formerly, and found it just as much as I did at first, which made me think I had not dried it sufficiently: then I put it into the oven twice more, after the bread was drawn, and weighed it the second time, but found it shrink little or nothing'" (*loc. cit.*, p. 65).

The obvious criticism of this experiment is that BOYLE failed to consider the atmosphere as a possible source of the increment in growth of his plant. He also failed to consider the possibility of soluble plant nutrients in his "good earth" and in the "spring water" used for irrigation. Since worms and insects seem to arise spontaneously from decaying plants, the transmuting power of water, through seminal or vitalistic agencies, was extended by BOYLE also to the animal and mineral kingdoms.

"It seems evident, that water may be transmuted into all the other elements; from whence it may be inferred, both, that 'tis not everything chymists will call salt, sulphur, or spirit, that needs alwaies be a primordiate and ingenerable body. And, that nature may contex a plant (though that be a perfectly mixt concrete) without having all the elements previously presented to her to compound it of. And, if you will allow the relation I mentioned out of Mounsieur DE ROCHAS to be true; then may not only plants, but animals and minerals too, be produced out of water. And however there is little doubt to be made, but that the plants my tryals afforded me, as they were like in so many other respects to the rest of the plants of the same denomination; so they would, in case I had reduced them to putrefaction, have likewise produced wormes or other insects, as well as the resembling vegetables are wont to do; so that water may, by various seminal principles, be successively transmuted into both plants and animals. And if we consider that not only men, but even sucking children are, but too often, tormented with solid stones; and that divers sorts of beasts themselves, (whatever HELMONT against experience think to the contrary) may be troubled with great and heavy stones in their kidneys and bladders, though they feed but upon grass and other vegetables, that are perhaps but disguised water, it will not seem improbable that even some concretes of a mineral nature, may likewise be formed of water.

"We may further take notice, that as a plant may be nourisht, and consequently may consist of common water; so may both plants and animals, (perhaps even from their seminal rudiments) consist of compound bodies, without having anything merely elementary brought them by nature to be compounded by them. . . ." (*loc. cit.*, pp. 188-9).

With regard to the residue of ash produced by the combustion of vegetable matter BOYLE suggests that this may also be produced by the transmuting action of the fire during incineration, as indicated in the following passage:—

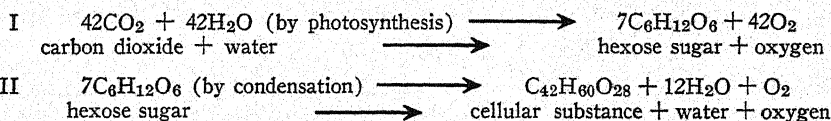
"I must next endeavour to make it probable, that the operation of the fire does actually (sometimes) not only divide compounded bodies into small parts, but compound those parts after a new manner, whence consequently, for ought we know, there

may emerge as well saline and sulphureous substances, as bodies of other textures" (*loc. cit.*, p. 76).

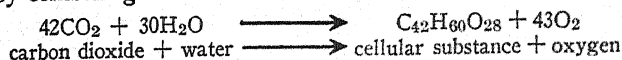
In his departure from the old doctrines of four elements and three principles BOYLE advocated a return to the corpuscular or atomic hypothesis of DEMOCRITUS as a more fruitful basis of experimentation. This view is expressed more definitely in his "Origin of Forms and Qualities according to the Corpuscular Philosophy" (1666). Water, not having been proved to be "made of any other bodies" in BOYLE's time, fulfilled his definition of an element and was so accepted.

"Water being esteemed an elementary body, and far more homogeneous than any other fluid; it will make very much for our purpose, to shew, that by a different texture of its parts, it may be brought to constitute bodies of very different qualities. And this it does by nourishing vegetables: for thus all, or the greatest part, of that which would accrue to a vegetable so nourished, appears to have been materially water; with what foreign quality soever it may afterwards, when transmuted, be endowed. HELMONT mentions an experiment of this nature, made with a willow, set in a pot of earth, which for several years he fed with rain-water. And we may conjecture at the easy transmutableness of water, by what happens in gardens and orchards, where the same showers of rain, after a long drought, cause a great number of differing plants to flourish. But these things do not fully reach our case, because it may be objected, that rain-water causes not these plants to thrive and flourish, by immediately affording them the aliment they assimilate into their own substance; but by proving a vehicle to the saline substances of the earth, itself being insensibly, afterwards, exhaled in vapour. And, indeed, experience shews us, that several plants, which thrive not well without rain-water, are not yet nourished by it alone; since when corn and fruit-trees have consumed the saline and sulphureous juices of the earth, they will not prosper there, how much rain soever falls upon the land, till by dung or otherwise, it be again supplied with proper juices. Wherefore I attempted to make plants grow in vials fill'd with nothing but water; and found, that *vinca peruviana*, *raphanus aquaticus*, spear-mint, and even *ranunculus*, grew and prosper'd very well therein; yet some of these were only slips without roots. Several were left in the water all the autumn, and a great part of the winter; and at the end of *January*, were taken out green, and with fair roots, which they had shot in the water: particularly a branch of *raphanus aquaticus*, was kept full nine months; and during that time withered not, tho' it pass'd the whole winter; and was taken out with many fibrous roots, some green buds, and an increase of weight. A stump of *ranunculus* prospered in the water so, that, in a month's time, it attained to more than double the weight it had when first put in. And another piece of *ranunculus* being taken out six months after it was put in, weighed almost a dram and an half, which was above thrice as much as it did at first: and this circumstance demonstrates a real assimilation and transmutation of water into the substance of the vegetable" (SHAW 1725, Vol. I, pp. 248-9).

BOYLE fails to mention whether rain or spring or river water was used in his experiments, although admitting that water may serve as a vehicle for saline substances. As we now know, the inference that the substance of vegetables is derived by "a real assimilation and transmutation of water" is only partially correct. Assuming that the organic cellular substance of wood contains 50 percent carbon, 6 percent hydrogen and 44 percent oxygen, which conforms to an approximate formula of $C_{42}H_{60}O_{28}$, we may express the phytochemical reactions by which the cellular substance of wood is formed as follows:



whence by combining I and II



From this it appears that 1012 parts by weight of cellular substance requires for its formation 540 parts by weight of water, so that VAN HELMONT and BOYLE, in assuming that water is the parent material from which the substance of vegetables is derived, were only about half right. It must be understood, however, that both VAN HELMONT and BOYLE had in mind an actual transmutation of water by the vital processes of the plant into carbon, mineral matter, etc., and this belief continued for over a century after the death of BOYLE.

Like DEMOCRITUS, BOYLE assumed that the ultimate particles, or corpuscles, of substances were of various shapes that affected the senses in different ways, but, unlike his Greek predecessor, he held that the particles were not indestructible but could be changed by attrition and other agencies. This is shown in his application of the corpuscular theory to the ripening of fruits:—

"After the fruit is gathered, and, being no longer a part of the tree, ceases, according to the most common opinion, to be a part of the living plant, it belonged to; yet it is very possible, that some fruits may receive maturation, after they have been severed from the plants that bore them. Apples, pluck'd too soon, usually obtain a mellowness by lying in heaps; which seems to be a kind, or degree of maturation; and medlars, gathered whilst they are hard and harsh, afterwards become soft, and better tasted. 'Tis also asserted by several writers of the affairs of *India*, that the fruit, they call *Bananas*, is usually gathered green, and hung up in bunches, in the house, where they ripen by degrees, and have an advantageous change made both of their colour, and tast. And this experiment, an ancient acquaintance of mine assured me, he had himself lately tried, and found to be true, in *America*. And indeed I see not, why a convenient degree of warmth, whether external from the sun and fire, or internal from some degree of fermentation, or analogous intestine commotion, may not put the sapid corpuscles into motion, and cause them, by various and insensible transursions to rub against each other, and thereby make the little bodies more slender and thin, less rigid or cutting, than they were before; and by various motions bring the fruit they compose to a state, wherein it is of a more soft consistence, and abounds in corpuscles less harsh, and more pliable, than formerly, and better fitted to the pores of the organs of tast; and, in a word, make such a change in the constitution of the fruit, as we express by the name of maturity. And that such mechanical changes of texture may much alter the qualities, and among them, the tast of a fruit, is obvious in bruised cherries and apples, which, in the contused parts, soon come to look and tast otherwise than they did before" (SHAW, Vol. I, p. 543).

Another application of the corpuscular theory to an agricultural chemical problem was made by BOYLE in explaining the unpleasant taste of butter:—

"I once, in *Savoy*, observ'd all the butter, that was made in some places, during the spring season, tasted very much of a certain weed, which, at that time, abounds in the fields there. And, considering how many elaborate alterations the rank corpuscles of this weed must have undergone, in the various digestions in the cow's stomach, heart, udder, &c. and that afterwards, two separations, at least, were made; the one of the cream from the rest of the milk; and the other of the unctuous parts of the cream, from the serum; it will scarce be deny'd, that vegetable corpuscles may, by association, pass thro' various disguises, without losing their nature; especially since the essential attributes of such corpuscles, may remain undestroy'd, tho no sensible quality survive, to make proof of it, as is afforded by our example in the offensive tast" (SHAW, Vol. 2, p. 233).

BOYLE also assumed that the ultimate corpuscles of different substances could combine by cohesion to form a new compound of higher complexity and of different nature. This is indicated in his explanation of the coagulation of milk by rennet:—

"Another cause of stability in bodies, is the admission of adventitious corpuscles into their pores: of the ways wherein this may happen, these appear to be the chief. 1. By expelling thence those voluble particles, which, by their shape, or motion, oppos'd the coalition, or disturb'd the rest of the other particles, whereof the body consisted. 2. By hindring the motion of the little bodies that compose it. And, 3. By constituting with the particles it consists of, corpuscles more unapt for motion, and fit for mutual cohesion. To these seems reducible the way of coagulating milk by rennet, whose saline particles pervading the body of that fluid, not only make a commotion in the parts of it, but fasten the branched particles thereof to one another, and, with them, constitute a body of another texture: when the weight of these curdled bodies, reducing them, by degrees into a closer order, squeezes out the thinner liquor, which the rennet was unable to coagulate; and which, being thus sever'd from the grosser parts of the milk, may well be more fluid than the milk itself" (SHAW, Vol. I, p. 331).

The value of applying experimental chemistry to the study of agricultural problems is emphasized by BOYLE in many of his writings, as in the following passages from his book upon, "Considerations touching the Usefulness of Experimental Natural Philosophy" (1663-71):—

"Chymical experiments may . . . afford useful directions towards the melioration of arable, pasture, and wood-land. From the experiments I, myself, have made upon earths, dungs, and seeds, whereby, I found, that salts abounded in the liquors they yielded; I see reason to wish this inquiry were farther prosecuted, towards the improvement of husbandry. Whoever has observ'd those many particulars in this art, which caused Sir FRANCIS BACON to pronounce nitre to be the life of vegetables; and, considers; how land is improved by pigeon's dung, which impregnates it with salt-petre; and, lastly, knows, that most fat earths, defended from the sun and rain, and left to themselves, will, soon, abound in nitrous salt; whoever, I say, considers these things, will, perhaps, believe an inquiry into the nature of salt-petre, may be of great use in farming.

"I, once, caused some earth to be dug up, from under a pigeon-house, and distilling it, in a retort, little, or no oil, but a considerable quantity of a reddish liquor came over; so far unlike spirit of nitre, that it greatly resembled volatile salts; for, without being rectified, it not only turn'd syrup of violets green, and precipitated a solution of sublimate, into a milky substance; but there, also, came over, therewith, into the lower part of the receiver, a dry salt, in taste like the volatile kind, and so far an alkali, that it readily hissed, and caused an ebullition in an acid menstruum. From hence, it seems which is highly remarkable, that a salt, very different from acid, may by the operation of the earth and air, be so alter'd as afterwards, by a slight management, to afford salt-petre, whose spirit is strongly acid. And dropping *Aqua fortis* upon pot-ashes, dissolv'd in a little fair water, 'till the ebullition and hissing were perfectly ceased; and having filter'd this liquor, and set it in an open vessel to evaporate, with a gentle heat; being, in two or three days time, removed to a cold place, it afforded very pure crystals of salt-peter.

"I might add, that the knowledge of the nature, and distinctions of saline bodies, may, greatly, assist, to shew the differences of the various saltiness that is found in soils; and with what sort each plant, or seed, is most delighted. By this means, many tracts of land, now thought barren, for want of a knowledge hereof, might be render'd useful. And ground may be made to yield much better crops, than usual, by being, successively, sown with a proper variety of seed, agreeable to the nature of the particular salt, at present, inherent in the earth; for, by the absence of one kind of salt, it is better prepared to feed those plants that delight in another. And of this, the husbandmen have, in some measure, already taken notice; as appears by their sowing turneps, in grounds too remote for the convenient carriage of compost, to serve for

manure, and fit them for wheat. And, I am of opinion, that any land, except mere sand, might, without much culture, be made fertile, were we but well acquainted with the soil, and provided of the various sorts of grain, that nature affords, in different countries. There are various soils, both in England, and elsewhere, left quite uncultivated, wherein some foreign vegetables might thrive and prosper" (SHAW, Vol. I, pp. 106-7).

"Chymistry and hydrostatics may help to discover the kinds and degrees of salt-ness, residing in several other bodies, the husbandman employs. I, myself, have made surprizing discoveries, in working upon some sorts of earth, by chymistry. And, as in particular, the fertility of manure, seems to depend upon it's salinophilous sulphureous parts; a practical inquiry into the differences and various operations of salts, may, probably, assist to discover various kinds of compost, with the proper manner, wherein to multiply, compound, and apply them" (*loc. cit.*, p. 108).

"I must here observe, that the more comprehensive any trade is, the more improvements it will admit of from philosophy; because, depending upon many natural productions and operations, there must arise many particulars to be meliorated, or reform'd, either in the manufacture, or profession. Thus corn, in husbandry, renders a knowledge of the whole art of tillage convenient, with the ways to order cattle, the dairy, an orchard, a kitchen-garden, wood, flax, hemp, hops, bees, &c. and the particular productions of some of these, as honey, cyder, &c. are capable of improvement, and require skill to manage. In the variety of particulars, therefore, wherewith the husbandman deals, there must be some, wherein the superior knowledge and experience of the naturalist, will be serviceable. And, as one of the principal parts of husbandry depends upon preserving cattle from diseases, and the fruits of the earth, from putrefaction; natural philosophy may conduce to both these ends. He who can accelerate, and delay putrefaction in bodies, may shew the husbandman how to prepare variety of manures; to enrich his ground with the peculiar kind of salt it wants; and, also, how to preserve several seeds, flowers, and fruits, beyond their natural duration. Thus many, by my recommendation, have continued fruits, as quinces, for instance, good, almost, all the year round, by a pickle made, only, of water, and the refuse of quinces, or what is easily obtain'd from them: but cherries I have preserved fresh and juicy for more than a year: and that without salt, or sugar, only by a proper spirit of wine, well impregnated with the tincture it drew from the skins of the same kind of fruit" (*loc. cit.*, pp. 108-9).

The student who turns from the pages of PARACELSUS and GLAUBER to those of BOYLE is immediately aware of a great improvement not only in the rejection of old fallacies and superstitions but in the adoption of a new motive of scientific inquiry and in the practice of a vastly more pleasing and amiable style of writing. BOYLE's copious sentences are sometimes fatiguing to those who love brevity; he is to be read, however, as much for literature as for science, and editorial revisions have usually injured the charming quality of his original text. The work of BOYLE was a turning point in the history of agricultural chemistry; although many of his theoretical views were afterwards disproved, he performed a lasting service by word and example in directing attention to the true aims and methods of experimental research.

The part which BOYLE played in helping to stimulate coöperative research among his contemporaries was also highly important. In 1645 he and a group of scientific friends founded an association known as the "Invisible College" whose chief purpose was the cultivation of the new experimental philosophy that had been proclaimed by Sir FRANCIS BACON. In forming this so-called college, BOYLE and his friends were no doubt inspired by BACON's imaginary sketch of a similar scientific society, "Solomon's House", described in the "New Atlantis". In 1660 the "Invisible College" was reorganized and two years later chartered under the new

name of the "Royal Society" under which designation it has continued to the present time.

The early Philosophical Transactions of the Royal Society contain numerous references to experiments, reports, inquiries, and proposals relating to agricultural chemical subjects. In the first volume of the Transactions, for July 3, 1665 (pp. 91-4), there is found under "Enquiries concerning Agriculture" a questionnaire for "those who are skilled in Husbandry", which is interesting because it contains one of the earliest suggestions of a comprehensive soil survey of a country. A few of the inquiries in this questionnaire are quoted:

"The several kinds of the soyls of England being supposed to be either Sandy, Gravelly, Stony, Clayie, Chalky, Light-Mould, Healthy, Marish, Boggy, Fenny, or Cold-weeping Ground; information is desired what kind of soyls your Country doth most abound with, and how each of them is prepared, when employed for Arable. 2. What peculiar preparations are made use of to these Soyls for each kind of Grain; with what kind of Manure they are prepared; when, how and in what quantity the Manure is laid on? . . . 4. How long the several Grounds are let lie fallow? . . . 6. What ground Marle hath over head? How deep generally it lieth from the surface? What is the depth of the Marle itself? What the colour of it? Upon what grounds it is used? What time of the year it is to be laid on? How many loads to an acre? What grains Marled land will bear and how many years to-gether?"

Except for the modification of a few archaisms the questionnaire is one that might still be used. References in the "Transactions" to the usefulness of changing seed yearly; to steeping, liming, and sowing seed in several ways; to preserving the vitality of seeds and freeing them from smut; and many other proposals indicate the deep interest of the first members of the Royal Society in the practical phases of agriculture.

The collaborative experiments of the Society, under the stimulating leadership of BOYLE and HOOKE, relate to many subjects of fundamental importance to agricultural chemistry, such as the basic problems of combustion and respiration. Among these may be cited experiments which demonstrate that there is no such thing

"as an elementary Fire of the Peripatetics; nor fiery Atoms of the Epicureans; but that Fire is only the Act of the Dissolution of heated sulphureous Bodies, by the Air as a Menstruum . . . that Heat and Light are two inseparable Effects of this Dissolution . . . and that Ashes are a Part of the Body not dissoluble by the Air" (SPRAT 1722, pp. 215-6).

Other experiments were designed

"to find the lasting of the burning of a Candle, Lamp, or Coals, in a cubic Foot of common, rarified, and condens'd Air"; "to try how long a Man can live by expiring and inspiring again the same Air; to try whether the Air so respired, might not by several Means be purified or renew'd"; to include "living Animals and kindled Coals, and Candles, in a large glass, to observe which of them will be first extinguish'd"; to demonstrate "the not growing of Seeds for want of Air"; "the growing of Plants hung in the Air and the Decrease of their Weight" (*loc. cit.*, pp. 216-9).

Observations were also made

"of the Growth of Vegetables in several Kinds of Water"; "of hindring the Growth of Seed Corn in the Earth, by extracting the Air and furthering their Growth by admitting it"; "of steeping Seeds of several kinds"; "of destroying Mites by several Fumes"; "of a Spider's not being enchanted by a Circle of Unicorn's Horn, or Irish

Earth, laid round about it"; and "of Flesh not breeding worms, when secur'd from Fly-blowing" (*loc. cit.*, pp. 222-3).

The last two experiments, as many others not cited, related to the testing of century old superstitions that were still current. Proposals for experiments of a more practical character related to the making of a fermented beverage from sugar-cane juice, to the fitness of various waters for making beer and ale, and to brewing beer with Ginger instead of hops.

BOYLE was a most voluminous writer, having been the author of over twenty works on chemical, physical and other scientific subjects and of over ten publications in the fields of philosophy and religion. While his important scientific discoveries, such as the inverse ratio of the volumes of gases to pressure (BOYLE's law), the rôle of air in the propagation of sound, the expansive force of freezing water, determinations of the specific gravities of substances, etc., were chiefly in the realm of physics, his favorite science was chemistry. He made, however, no important discoveries in chemistry, his work in this science being largely speculative.

Owing to his great charm of manner and congenial disposition BOYLE was a source of continued inspiration to all his scientific associates. The Royal Society was most fortunate, at the time of its inception, in having so sympathetic a leader as BOYLE to conduct its members in the pursuit of collaborative research.

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Francesco Redi (1626-97): — A close contemporary of ROBERT BOYLE was FRANCESCO REDI, a celebrated Italian chemist, physician and entomologist. He was not a member of the Royal Society but his work on the quantity and character of the ash constituents of over thirty different plant products so impressed its members that an abstract of his pioneer investigations in this field was published in Vol. 20 of the *Philosophical Transactions* (pp. 281-9). Although this publication did not appear until 1698, REDI's plant ash investigations were performed largely in the year 1660, which antedated GREW's paper on the lixivial salt of plants by 16 years. The following summary is given of REDI's observations on the preparation and examination of plant ashes:

Pounds.	<i>Vegetables.</i>	<i>Ashes.</i>			<i>Salts.</i>		
		lb	3	3	lb	3	3
100	Of dried Flowers of Oranges	4	06	00	00	00	05
800	Of Gourds new gathered which dried in the Oven were 36 lb	4	00	00	00	10	00
400	Red Onions (being 720) roasted, the Coals turn'd to 16 lb to the Coals new added 4 $\frac{3}{4}$ of Sulphur.	1	06	00	00	02	02
150	Eyebright fresh, and afterwards stilled and burnt	5	00	00	00	04	00
120	Distill'd Roses	4	00	01			
100	Of Maidenhair	9	00	00	00	00	04
150	Roots of Black Hellebore, which dried came to 50 lb	6	00	00	00	01	00
150	Roots of White Hellebore fresh, which dried came to 50 lb	2	00	00	00	04	00
96	Roots dried and burnt of fresh Ecula	3	00	00	00	02	00
30	Roots of Liquorish	2	00	00	00	01	04
20	Pellitory	1	00	00	00	00	06
100	Green Endive	2	00	00	00	02	00
90	Green Bindweed	1	00	00	00	02	00
2000	Leaves of Lawrel	33	00	04	00	00	00
500	Leaves of Lawrel	6	00	00	00	10	00
1000	Water Mellons well ripe, the Seeds being taken	25	00	01	00	09	00
2400	Cucumbers	18	00	00	00	00	00
300	Wood of Ivy	9	00	00	00	00	00
50	Scorzonera dried	8	00	00	00	00	00
300	Pine Apples, the Nuts taken out	3	00	00	00	00	00
150	Mugwort dried	8	00	00	00	00	00
130	Leaves of Cyprus	6	00	00	00	00	00
10	Peele of Pomgranates dried	08	00		00	00	00
2	Sassafras	00	00		00	00	00
12	<i>Lignum Sanctum</i>	2	06	00	00	00	00
4	Yellow Sanders	01	04		00	00	00
4	Black Pepper	02	04		00	00	00
30	Ginger	1	07	00	00	00	00
12	Turbith	1	00	00	00	00	00
	Wood of Firr	3	00	00	00	03	00
	Scopæ	16	00	01	00	04	00
	Scopæ	16	00	01	00	06	00

Heads.

A weighed amount of the herb, flowers, fruit, wood or other plant material is burned to an ash. The ash is weighed and then treated with about five parts of pure water at ordinary temperature. When no more ash is dissolved the solution is filtered and the filtrate, which should be clear, is evaporated in a glass evaporating dish on a hot water bath, to the concentration which is most favorable for the crystallization of the mixture of salts. Glazed earthenware evaporating vessels should not be used, as the salty solution will attack the coating. The extracted ashes if burned again in a brick furnace will usually give a small additional amount of soluble salts.

The soluble salts obtained by this process are deliquescent in moist air and if it is desired to avoid this difficulty REDF recommended mixing the plant material before incineration with sulphur. Four or five ounces of sulphur to 100 lbs. of plant material is considered to be about the proper proportion. The salts obtained by this method of preparation will not deliquesce and will remain white and crystalline.

Mixed salts, as of copper vitriol, alum and nitre, when dissolved, can be recovered again on careful evaporation in their natural crystalline forms. The salts obtained from the ashes of different plant materials show a variety of such forms, thus lettuce, musk-melon, black hellebore, endive, worm-wood, sorrel, and shoots of vines yielded two sorts of crystals; black pepper and incarnate rose three sorts; and roots of white hellebore four sorts. In all these mixtures of salts cubical crystals were always observed. Different parts of the same plant yield salts of different crystalline appearance. Thus the salt of the leaves of laurel differs in appearance from the salt of laurel wood; the salt of the pulp of a gourd differs from that of its rind. Many of the salts from different plant materials resemble one another in appearance. Thus the salt from cucumbers resembles that from lettuce. The salts from orange flowers, roses, ginger, endive, white hellebore roots and liquorish are like one another. Each kind of salt retains its own peculiar form, however often dissolved in water and recrystallized.

To separate each individual kind of salt from the mixture occurring in plant ashes, great care must be exercised during evaporation of the solution. If evaporation is conducted too far the salts all crystallize out together as a confused mass; if the solution is too weak crystallization is very slow. The proper concentration can only be learned with long practice. Specific gravity determinations may be of some help in controlling the process. When the solutions have been reduced to the proper concentrations they are transferred to stoppered glass vessels and set aside in a dry shady place when in the course of time crystals will form on the bottom or sides of the vessel.

The quantities of ashes and of salts obtained from different plant materials vary according to the differences in species, and in the season of the year and locality in which the plants are gathered.

The remainder of the article discusses the purgative action of the salts obtained from different plant ashes, this having been the primary purpose of REDF's investigation. He noted no difference in physiological action between the salts of different crystalline form from the ashes of various plants. The cubical blunt crystals acted no differently from those with sharp points. He concluded that the salts from the ashes of herbs, flowers, fruits, etc. do not possess the peculiar medicinal properties that physicians attribute to the original plant material.

According to the table which accompanies the abstract of REDF's work the quantity of plant material which he took for his incinerations varied from 2 lbs. in the case of sassafras to 2400 lbs. in the case of cucumbers. In another table the weights (apothecary) of ashes are recalculated to 100 lbs. of plant material. REDF's results, when calculated to a percentage basis, show in general as good an agreement with present day findings as could be expected, considering the differences in methods of analysis and the natural variations in ash content of the various plant materials. REDF's table which is here reproduced is of great historic interest as it is the prototype of all subsequent plant ash compilations. No further advancement was made in this field until the publication of DE SAUSSURE in 1804, who made the first attempts to determine the chemical composition of different plant

ashes — an undertaking that was impossible of attainment in REDI's time owing to the undeveloped state of chemical analysis.

REDI is chiefly remembered by historians of science for his disproof of the long prevalent belief that maggots were generated spontaneously in putrid meat. His carefully conducted experiments of 1668 showed conclusively that when flies were prevented from depositing their eggs in the meat no larvae were produced.

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Robert Hooke (1635-1703):— Among the various members of the newly organized Royal Society, the most ingenious in the performance of experiments was ROBERT HOOKE. He was born at Freshwater on the Isle of Wight and obtained his education at Westminster School and Oxford. His mechanical ability was recognized in 1655 by BOYLE who obtained HOOKE's aid in the construction and operation of his air pump. In 1662 he was appointed curator of experiments for the Royal Society, was elected one of its fellows in 1663 and served as its secretary from 1677 to 1683. Although his technical skill and inventiveness were greatly appreciated by his colleagues, HOOKE's virulent outbreaks of temper and unsocial habits made him at times a disagreeable companion. His contributions to science were of a most varied character and anticipated, although imperfectly, many later discoveries such as the law of gravitation, the undulatory theory of light, the doctrine of interference, the composition of the atmosphere and its function in respiration and combustion. He first proposed the use of the pendulum as a measure of gravity, invented the wheel barometer and other instruments of precision, and was among the earliest to apply barometrical observations to forecasting the weather. His great diversity of interests prevented him, however, from carrying any single investigation through to completion and so it has been said of him that "he originated much but perfected little."

HOOKE's experimental investigations are published in the early *Philosophical Transactions of the Royal Society*. His best known work is the "*Micrographia or some Physiological Descriptions of Minute Bodies made by Magnifying Glasses with Observations and Inquiries thereupon*" published at London with the imprimatur of the Royal Society in 1665. Using minute lenses of his own manufacture HOOKE constructed high power microscopes with which he investigated crystals; vegetable fibers; sections of leaves, seeds and other plant organs; fungi; hair; feathers; insects; vinegar eels; and other forms of microscopic life. Interspersed among his descriptions of these objects are numerous observations, frequently of a chemical character, upon the constitution and properties of matter. HOOKE's theory of combustion is thus described in his "Observation XVI. Of Charcoal or burnt Vegetables":—

"From the Experiment of charring of Coals (whereby we see that notwithstanding the great heat, and the duration of it, the solid parts of the Wood remain, whilst

they are preserv'd from the free access of the air undissipated) we may learn, that which has not, that I know of, been publish'd or hinted, nay, not so much as thought of, by any; and that in short is this.

"First, that the Air in which we live, move, and breath, and which encompasses very many, and cherishes most bodies it encompasses, that this Air is the menstruum, or universal dissolvent of all Sulphureous bodies.

"Secondly, that this action it performs not, till the body be first sufficiently heated, as we find requisite also to the dissolution of many other bodies by several other menstrooms.

"Thirdly, that this action of dissolution, produces or generates a very great heat, and that which we call Fire; and this is common also to many dissolutions of other bodies, made by menstrooms, of which I could give multitudes of Instances.

"Fourthly, that this action is perform'd with so great a violence, and does so minutely act, and rapidly agitate the smallest parts of the combustible matter, that it produces in the diaphanous medium of the Air, the action or pulse of light, which what it is, I have else-where already shewn.

"Fifthly, that the dissolution of sulphureous bodies is made by a substance inherent, and mixt with the Air, that is like, if not the very same, with that which is fixt in Salt-peter, which by multitudes of Experiments that may be made with Saltpeter, will, I think, most evidently be demonstrated.

"Sixthly, that in this dissolution of bodies by the Air, a certain part is united and mixt, or dissolv'd and turn'd into the Air, and made to fly up and down with it in the same manner as a metalline or other body dissolv'd into any menstrooms, does follow the motions and progresses of that menstruum till it be precipitated.

"Seventhly, that as there is one part that is dissoluble by the Air, so are there other parts with which the parts of the Air mixing and united, do make a Coagulum, or precipitation, as one may call it, which causes it to be separated from the Air, but this precipitate is so light, and in so small and rarify'd or porous clusters, that it is very volatil, and is easily carry'd up by the motion of the Air, though afterwards, when the heat and agitation that kept it rarify'd ceases, it easily condenses, and com-mixt with other indissoluble parts, it sticks and adheres to the next bodies it meets withall; and this is a certain Salt that may be extracted out of Soot.

"Eighthly, that many indissoluble parts being very apt and prompt to be rarify'd, and so, whilst they continue in that heat and agitation, are lighter then the Ambient Air, are thereby thrust and carry'd upwards with great violence, and by that means carry along with them, not onely that Saline concrete I mention'd before, but many terrestrial, or indissoluble and irrefeable parts, nay, many parts also which are dissoluble, but are not suffer'd to stay long enough in a sufficient heat to make them prompt and apt for that action. And therefore we find in Soot, not onely a part, that being continued longer in a competent heat, will be dissolv'd by the Air, or take fire and burn; but a part also which is fixt, terrestrial, and irrefeable.

"Ninthly, that as there are these several parts that will rarifie and fly, or be driven up by the heat, so are there many others, that as they are indissoluble by the aerial menstruum, so are they of such sluggish and gross parts, that they are not easily rarify'd by heat, and therefore cannot be rais'd by it; the volatility or fixtness of a body seeming to consist only in this, that the one is of a texture, or has component parts that will be easily rarify'd into the form of Air, and the other, that it has such as will not, without much ado, be brought to such a constitution; and this is that part which remains behind in a white body call'd Ashes, which contains a substance, or Salt, which Chymists call Alkali: what the particular natures of each of these bodies are, I shall not here examine, intending it in another place, but shall rather add that this Hypothesis does so exactly agree with all Phaenomena of Fire, and so genuinely explicate each particular circumstance that I have hitherto observ'd, that it is more than probable, that this cause which I have assign'd is the true adequate, real, and onely cause of those Phaenomena; And therefore I shall proceed a little further, to shew the nature and use of the Air.

"Tenthly, therefore, the dissolving parts of the Air are but few, that is, it seems of the nature of those Saline menstrooms, or spirits, that have very much flegme mixt with the spirits, and therefore a small parcel of it is quickly glutted, and will dissolve no more; and therefore unless some fresh part of this menstruum be apply'd to the body to be dissolv'd, the action ceases, and the body leaves to be dissolv'd and

to shine, which is the Indication of it, though plac'd or kept in the greatest heat; whereas Salt-peter is a menstruum, when melted and red-hot, that abounds more with those Dissolvent particles, and therefore as a small quantity of it will dissolve a great sulphureous body, so will the dissolution be very quick and violent.

"Therefore in the Eleventh place, it is observable, that, as in other solutions, if a copious and quick supply of fresh menstruum, though but weak, be poured on, or applied to the dissoluble body, it quickly consumes it: So this menstruum of the Air, if by Bellows, or any other such contrivance, it be copiously apply'd to the shining body, is found to dissolve it as soon, and as violently as the more strong menstruum of melted Nitre.

"Therefore twelfthly, it seems reasonable to think that there is no such thing as an Element of Fire that should attract or draw up the flame, or towards which the flame should endeavour to ascend out of a desire or appetite of uniting with that as its Homogeneous primitive and generating Element; but that that shining transient body which we call Flame, is nothing else but a mixture of Air, and volatil sulphureous parts of dissoluble or combustible bodies, which are acting upon each other whilst they ascend, that is, flame seems to be a mixture of Air, and the combustible volatil parts of any body, which parts the encompassing Air does dissolve or work upon" (*Micrographia*, pp. 103-5).

In sections five and six of the above quotation HOOKE has anticipated to a remarkable degree the discoveries of over a century later upon the rôle of the atmosphere in the burning of combustible bodies. The "substance inherent and mixt with the Air, that is like, if not the very same, with that which is fixt in Salt-peter" is of course now referred to the gaseous element oxygen and the certain part of the combustible substance which in burning "is united and mixt, or dissolv'd and turn'd into the Air" would now be interpreted as the constituent elements (hydrogen and carbon) that are converted into water vapor and carbon dioxide. HOOKE's doctrine of combustion is essentially the same as that adopted several years later by MAYOW. In the statement of section twelve that fire is not an element but simply "a mixture of Air and the combustible volatil parts of any body" HOOKE was also in advance of his time.

In January 1663, previous to the completion of the *Micrographia*, HOOKE performed before the Royal Society an

"experiment of shutting up in an oblong glass a burning lamp and a chick; and the lamp went out within two minutes, the chick remaining alive" (*BIRCH*, Vol. I, p. 180).

In January 1665, while his book was in press, it is recorded that

"Mr. HOOKE made an experiment tending to show, as he conceived, that air is the universal dissolvent of all sulphureous bodies, and that this dissolution is fire; adding that this was done by a nitrous substance inherent and mixt with the air" (*loc. cit.*, Vol. II, p. 2).

which is a quotation in part of the language of the *Micrographia*. The relationship of rarified and compressed air to combustion and respiration is indicated by other experiments conducted two weeks later (*loc. cit.*, II, p. 10). At a meeting of the Society on June 7, 1665

"Mr. HOOKE reported that he had sown some lettuce seed upon earth in the open air; and at the same time upon other earth in a glass-receiver, which was afterwards exhausted of air; that the seed exposed to the air was grown up an inch and an half high within eight days; but that in the exhausted receiver not at all; both which were produced and shewn the Society" (*loc. cit.*, II, p. 54).

Experiments reported before the Society by Hooke in December 1667 "seem to hint that the foetus in the womb has its blood ventilated by the help of the dam" (*loc. cit.*, II, p. 232) and in April 1668 "that some mixture of air in the blood in the lungs might give that floridness" (*loc. cit.*, II, p. 274) which is the characteristic color of arterial blood. These and other passages, which might be cited, show that the idea of a relationship between the phenomena of combustion, germination, respiration, etc., had taken a firm hold upon the minds of Hooke and other members of the Royal Society. In the performance of experiments Hooke displayed much originality. Gases were collected not only in bladders but in glass vessels inverted over water, so that Hooke might be called one of the earliest experimenters to construct a pneumatic trough.

Although Hooke made free use of conjectures, they were usually qualified and never stated dogmatically. This is well illustrated in the expression of his views upon spontaneous generation. In his "Observation XX. Of blue Mould, and of the first Principles of Vegetation arising from Putrefaction" he announced that

"Mould and Mushrooms require no seminal property, but the former may be produc'd at any time from any kind of putrifying Animal, or Vegetable Substance, as Flesh, &c. kept moist and warm . . ." (*Micrographia*, p. 127).

The same view is restated in his "Observation XIX" where he affirms it to be "very much the method of nature" for putrefying vegetable and animal substances to produce vegetables and animals of a lower order, although a little later he partially reopens the question by suggesting a modified alternative explanation:—

"or perchance some kind of Insect, in such places where such kind of putrifying or fermenting bodies are, may, by a certain instinct of nature, eject some sort of seminal principle, which cooperating with various kinds of putrifying substances, may produce various kinds of Insects, or Animate bodies: For we find in most sorts of those lower degrees of Animate bodies, that the putrifying substances on which these Eggs, Seeds, or seminal principles are cast by the Insect, become, as it were, the Matrices or Wombs that conduce very much to their generation, and may perchance also to their variation and alteration . . ." (*loc. cit.*, p. 123).

Hooke's writings were a great stimulus to the scientific work of the following generation. He recognized most clearly the limitations of human effort and few worthier sentiments have been expressed by a scientist than the one contained in the noble Preface of his *Micrographia*:—

"As for my part, I have obtained my end, if these my small Labours shall be thought fit to take up some place in the large stock of natural Observations, which so many hands are busie in providing. If I have contributed the meanest foundations whereon others may raise nobler Superstructures, I am abundantly satisfied; and all my ambition is, that I may serve to the great Philosophers of this Age, as the makers and the grinders of my Glasses did to me; that I may prepare and furnish them with some Materials, which they may afterwards order and manage with better skill, and to far greater advantage."

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John Mayow (1643-79):—JOHN MAYOW was born at London in May 1643 and, after his preliminary school training, entered Wadham College, Oxford, at the age of fifteen. In 1660 he was elected to a fellowship at All Souls College from which he was graduated as a bachelor-in-law in 1665 and as a doctor-in-law in 1670. Medicine, however, was MAYOW's chief interest and he made this subject, and not law, his profession. He was interested especially in respiration and published a tract upon this subject at Oxford in 1668. MAYOW's "Five Medico-physical Treatises", published in Latin at Oxford in 1674, contains his best known chemical work "De Sal-Nitro et Spiritu Nitro-aereo" (on Sal-nitre and nitro-aereal Spirit). MAYOW was a friend of HOOKE, whose investigations before the Royal Society on combustion and respiration undoubtedly exerted a strong influence on the development of his own ideas.

MAYOW's attempt to construct a rational synthesis of existing opinions regarding combustion, respiration and other related phenomena is one of the most interesting illustrations in the history of science of how near a speculative mind upon the basis of observation and experiment can approach the discovery of truth without actually perceiving it.

He begins his discussion with saltpeter, about which GLAUBER and other chemists had written so much,

"as if, indeed, it were ruled by fate that this wonderful salt should make no less noise in philosophy than in war, and fill the universe with its sound" (*Alembic Club Reprint 17, p. 1*).

Nitre when decomposed yields an acid spirit (*i.e.*, nitric acid) and a residue of alkali.

"If the acid spirit of nitre is poured upon any alkali, or, in place of the alkali, upon purely saline volatile salt (*i. e.* ammonium carbonate), from the neutral strife of these two things coming together and the intense action, *sal nitrum* is generated, which will readily deflagrate when thrown into the fire" (*loc. cit.*, p. 3).

The common principle in air and in nitre, which promotes combustion, is termed by MAYOW the nitro-aërial or igneo-aërial spirit:—

"The constituents of nitre having been in this way considered, let us next inquire how *sal nitrum* is produced in the earth. For from almost any soil impregnated by the air and the weather, but especially from such as abounds in sulphur and fixed or volatile salt, as that from stables, dovecots, and slaughter-houses, *sal nitrum* is abundantly derived, and from its source is well called *sal terrae*.

"As to the mode in which nitre originates in the earth, the generally received opinion is that the earth as its proper matrix draws *sal nitrum* from the air in virtue of its own attractive force. And, indeed, there can be no doubt whatever that the air contributes in no small degree to the generation of nitre, since nitre is only evolved from soil which is impregnated with air. Moreover, if earth from which all nitre has been lixiviated be exposed to the air, it will after some lapse of time abound once more in nitre" (*loc. cit.*, p. 3).

"Let us consider then, in the next place, what part of the nitre is contributed by the earth, and, also, what is contributed by the air. With regard to this, it is our opinion that the fixed salt of which nitre in part consists, is derived from the earth—and for this reason, that it cannot, as we have already indicated, reside in the very rare air on account of its highly fixed nature. It favours this view that from earth

impregnated with fixed or volatile salt, as from stables and also from soil containing quicklime or ashes, *sal nitrum* is lixiviated in greater abundance than from any other soil, because these salts, united in course of time with nitro-aërial spirit in a way to be explained below, are converted into nitre. And, indeed, it is probable that ashes, quicklime, and the like fertilise the soil, for this reason only, that they afford fixed salt for the production of nitre, as will be shown below.

"Here, perhaps, some one will object that if earth from which all the salts have been lixiviated is exposed to the air, *sal nitrum* will, after some time, be produced in it anew.

"I reply that seeds of fixed salts exist, although obscurely, in all soil, even in that which has been lixiviated, and that these, by the force of a sort of aërial ferment, are digested in course of time into fixed salt, as I shall endeavour to show below. That the earth is impregnated with a certain universal seed, fecundating all things, has long been a received opinion. Why, then, not suppose that this macrocosmic seed is either itself fixed salt or, at least, the seeds of fixed salts hidden in the bosom of the earth; and that these when brought in progress of time to maturity are, together with nitro-aërial spirit, changed into *sal nitrum*. And it is a proof of this that nitre generated in the bowels of the earth contributes in no small degree to the growth of plants, as will be shown below. For as metallic seeds here and there dispersed through the mass of the earth are in the course of time converted into perfect metals, it is in like manner probable that seeds of fixed salts lie deep hidden in every fertile soil as in a suitable matrix, and that they by long digestion and the influx of air are changed into fixed salts. For in no other way can we conceive whence there should arise such an abundance of fixed salts as is usually obtained by lixiviation from the ashes of burned plants. For certainly none of these salts can proceed from another source than the earth . . ." (*loc. cit.*, pp. 4-6).

"From what has been said we can see why animal excreta, salts of lye and also quicklime, and similar substances imbued with fixed salts fertilise the soil. Indeed the saline-sulphureous excreta of animals, as also fixed salts in union with terrestrial sulphur, are specially adapted for effervescing with nitro-aërial spirit, and they also supply appropriate material for the production of nitre and consequently contribute not a little to the production of plants.

"Thus then the so much talked of fermentation, by which the numerous family of plants is produced from the bosom of the earth, appears to be nothing else but the internal motion of nitro-aërial particles when they meet with the sulphur and salt of the earth, in virtue of which terrestrial nitre is produced and the sulphur brought to a suitable volatility.

"It follows from what has been said that the salts of which plants are composed are to some extent nitrous and not purely saline, as we intimated above. For all vegetable salts are derived either from the air or from the earth. As regards the air it is by no means to be supposed that an alkaline and fixed salt resides in it; nor is the earth impregnated with a purely saline salt, for only nitrous salts can be extracted from it by lixiviation. And hence we may conclude that the salts of plants are nitrous and not purely saline: Hence in soil on which plants grow abundantly no nitrous salt is to be found, the reason being that all the nitre of the soil is sucked out by the plants. But when plants are calcined to ashes, the acid spirit of the nitre of which they are composed goes off as vapours, while the other element of the nitre—to wit, the alkaline salt—is left in the ashes . . ." (*loc. cit.*, pp. 38-9).

"Nor should it be overlooked that the nitre innate in plants contributes not a little to their burning, and that those which abound the most in nitrous particles take fire at once, even when they are green and full of moisture. Among these the ash is especially remarkable, for be it ever so green it yet burns with a bright flame. But, indeed, its richness in nitre may be inferred from the fact that while burning it gives out, from time to time, cracks like kindled nitre . . ." (*loc. cit.*, p. 41).

"The mode in which the structure of things is most speedily dissolved is Fire. But this is nothing else than an exceedingly impetuous fermentation of nitro-aërial and sulphureous particles in mutual agitation, as has been shown above. Thus, in combustion, sulphureous particles, moving with extreme velocity, throw into a most violent and fiery motion the nitro-aërial particles which exist in a state of fixation. This is evident when nitre is burned, for in its burning, nitro-aërial particles which were previously fixed and inert in the embrace of the fixed salt, are thrown into fiery

motion by the agency of the sulphureous particles. And indeed it is probable that even the nitro-aërial particles of the air are in a fixed state previous to their being roused into fiery motion, as I shall endeavour to show elsewhere.

"As the destructive power of fire is due to nitro-aërial particles, so also every internal movement which things undergo seems to depend upon a less violent agitation of the same particles. And it is a proof of this that in putrefaction and in nearly all fermentative movements some heat is excited, and this must be supposed to result from the motion of nitro-aërial particles, as will be shown immediately. How great moreover is the resemblance and affinity between fire and all other fermentations will appear from what follows.

"With regard to fire, it is to be noted that for the burning of things, it is necessary that nitro-aërial particles should either be already in the burning substance or be supplied from the air. Gunpowder burns very readily on account of the nitro-aërial particles it contains; plants burn partly from the nitro-aërial particles they contain, and partly from such as come from the air; but sulphureous matter, pure and simple, can only be ignited by nitro-aërial particles supplied by the air.

"And, just as for the production of fire, so also for exciting fermentations in plants, both sulphureous and nitro-aërial particles must either exist in the things to be fermented or be supplied from without. The juice expressed from plants, such as the must of wine or of apples and the like, effervesces on account of the nitro-aërial and sulphureous particles which it contains. For we have shown above that nitrous salts and therefore also nitrous-aërial particles are contained in most plants, though, at the same time, the nitro-aërial spirit supplied by the air contributes much to the fermentation of these liquids, for very warm weather intensifies the action in no small degree. Further, that the fermentation of the aforesaid liquids, as also of all things whatsoever, is due to the mutual agitation of nitro-aërial and saline-sulphureous particles, is evident from the fact that liquids of this kind, and indeed nearly every thing, become sour in fermenting; for it has been shown above that acidity is caused by the action of nitro-aërial spirit. Should any one be inclined to think that the fermentation of the said liquids ought not to be classed among effervescences with a destructive tendency, I reply that although the juices expressed from plants become more perfect by fermentation so far as their use to man is concerned, yet, in respect to the compound whose structure it impairs, the aforesaid effervescence is rightly called destructive.

"But when the decay of things is caused by extraneous heat and moisture, the internal movement is mainly effected by nitro-aërial particles supplied by the air. For nitro-aërial particles abound in a moist warmth; for we must suppose that heat of all kinds is due to their motion. When therefore nitro-aërial particles enter any substance along with extraneous moisture, they engage in conflict with the saline-sulphureous particles which they meet, and in consequence of their mutual agitation the structure of the compound is dissolved. Hence such things as exclude nitro-aërial spirit protect substances from corruption. And this is the reason why vegetable fruits, and even flesh, when covered with butter are preserved for a long time from putrefying . . ." (*loc. cit.*, pp. 42-4).

If the word "oxygen" be substituted for "nitro-aërial spirit" and the word "combustible" for "sulphureous", it might be supposed that most of the passages just quoted from MAYOW were taken from some modern chemical treatise. Indeed, it has seemed to some writers that combustion, oxidation, respiration, nitrification, acidification, fermentation, decay and many other phenomena, about which men had been speculating for centuries, were first intelligently explained by MAYOW and that he thus anticipated the later discoveries of PRIESTLEY and LAVOISIER. These commentators, misled by certain apparent parallelisms, have no doubt erred in applying to some of their readings of MAYOW interpretations that he did not have in mind. On the other hand detractors, who belittle everything that MAYOW accomplished, have gone to the opposite extreme.

While the rôle of MAYOW's "nitro-aërial" spirit seems to coincide in many respects with that of the element oxygen, his own conception of

the nature of this hypothetical entity, because of the existing very undeveloped state of chemistry, was something very different. Adopting the atomic hypothesis of DEMOCRITUS, as revived by BACON and BOYLE, MAYOW conceived the minute corpuscles of air to be of a complex nature consisting of a combination of aërial and nitro-aërial particles: —

"It would certainly be reasonable to suppose that nitro-aërial and fiery particles are fixed in the aërial particles themselves and constitute the more active part of them. For although aërial particles are very minute and are commonly regarded as most simple and elementary, still it seems to me necessary to suppose that they are compound and that some of their parts are branchy and adhere firmly to each other as if by mutually clasping hooks; while others are extremely subtle, solid, smooth, agile, fiery and truly elementary, and that these when firmly fixed among the other particles make them rigid . . ." (*loc. cit.*, p. 79).

"To this I add further that the rigidity of aërial particles appears to contribute not a little to the kindling of fire inasmuch as the nitro-aërial particles on being violently torn from the particles of the air in which they were firmly fixed are thrown into very rapid motion, for otherwise I do not see how the nitro-aërial particles could begin so rapid a movement . . ." (*loc. cit.*, p. 80).

"Further, it is a reasonable supposition that the aërial particles, deprived in the manner aforesaid of nitro-aërial particles, become not only unfit for sustaining fire but also change from rigid to flexible and in consequence are deprived of their elasticity, for that the rigidity of aërial particles is due to nitro-aërial particles fixed in them, while their elasticity results from their rigidity, I have already endeavored to show . . . fire seems to be nothing else than a collection of very minute sparks very densely struck out from aërial particles by the collision of sulphureous particles . . ." (*loc. cit.*, p. 81).

"I add further in confirmation of what has been said, that the nitro-aërial particles to which the elastic force of the air is due are fixed in the aërial particles themselves and are torn from them by the burning of a lamp or by the breathing of animals; for that the nitro-aërial and elastic particles which are lacking in the aforementioned glass vessels are neither air itself nor some material interspersed among its particles, has been shown above, and therefore it must be concluded that the elastic particles are implanted in the particles of the air themselves and constitute their more active part, and that it is in fine because these are driven out from the aërial particles by the burning of fire or by the breathing of animals that air becomes quite effete and destitute of elastic force . . ." (*loc. cit.*, p. 82).

"It is thus evident that the igneo-aërial particles common to nitre and air are not air itself, but only certain very subtle particles which fixed in air and in nitre constitute their more active and fiery part. Indeed it is probable that igneo-aërial spirit is fixed in the saline particles of nitre very much in the same way as in the aërial particles, and that it is in consequence of their being violently torn from both kinds of particles and thrown into violent agitation that fire is produced.

"It will not be difficult to understand from this hypothesis of ours why the water ascends in a glass in which a lamp or an animal is enclosed, although air exists in it in the same abundance as before, and there is no reason to suppose that it has condensed. For no other conception is possible than that the elastic force of the air has been diminished, and that this is due to a certain change wrought in the aërial particles themselves. But what that change should be, which diminishes the elastic force of the air, unless we suppose that the particles from being rigid become flexible, I confess that I do not understand" (*loc. cit.*, p. 84).

Fire, according to MAYOW, is then due not to a combination of his nitro-aërial particles with combustible matter as we now understand but to their being struck out from their aërial combination: —

"The sulphureous particles of a lamp contribute in no way to produce flame, except in so far as they strike out from aërial particles, the nitro-aërial particles" (*loc. cit.*, p. 137).

When this happens air loses something of its elasticity or spring and hence the slight contraction in volume when a lamp burns under an inverted vessel over water. PHILO OF BYZANTIUM, as we have seen, performed this same experiment over 1800 years before and explained it as due to the conversion of air particles into finer fire particles which escaped through the pores of the glass. ROBERT FLUDD described the same experiment in his "De Macrocosmi Historia" (1617, p. 471) and VAN HELMONT also mentioned it in his "Ortus Medicinæ"; both of these authors attributed the contraction in volume to a consumption of part of the air. The true explanation of this classic experiment was not given until many years later.

MAYOW assumed that his nitro-aërial particles after being struck out of combination either in air, or nitre, were powerless to participate in combustion or respiration. In this inert state they filled all space but were reactivated by solar energy in the upper atmosphere where recombination with the residual air particles took place. The compound particles thus reconstituted sank by their heavier weight to the lower regions of the atmosphere, where they could once again participate as promoters of respiration and combustion; in this way MAYOW supposed the cycle to be restored and made continuous.

It will be seen that the speculations of MAYOW, although highly ingenious, remove him at once from consideration as a discoverer of oxygen or of the train of important phenomena connected with oxidation. That he came surprisingly close to a true explanation of many facts must be admitted. His scientific contemporaries recognized his ability as a thinker and experimenter by electing him on the proposal of HOOKE a Fellow of the Royal Society in 1678. He died the following year at the early age of thirty-six and had his life been spared he could no doubt have brought his early conjectures upon combustion, respiration, and fermentation to a state of greater perfection.

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Nehemiah Grew (1641-1712):— One of the most active of the early members of the Royal Society was the celebrated plant anatomist and physiologist, Dr. NEHEMIAH GREW. He was born in Warwickshire, England, graduated at Cambridge, took his M.D. degree at Leyden in 1671 and then began the practice of medicine in London. His interest in plant anatomy was first awakened in 1664. The early results of his studies were submitted in 1670, under the title "The Anatomy of Vegetables Begun", to the Royal Society, which approved of the work and ordered its publication in 1671. In 1672 the Society published a similar work "Anatome Plantarum", by the Italian physiologist MARCELLO MALPIGHI (1628-94). GREW, having been rewarded by the Royal Society in 1672 by appointment as Curator on the Anatomy of Plants, was requested to continue his studies and progress was reported in a series of lectures between 1673 and 1677.

The enlarged work was then assembled and published in 1682, with the imprimatur of the Royal Society, as "The Anatomy of Plants with an Idea of a Philosophical History of Plants and several other Lectures Read before the Royal Society. By NEHEMIAH GREW M.D. Fellow of the Royal Society, and of the College of Physicians". This folio volume of 304 pages, with 83 finely engraved plates of microscopic drawings of plant organs, sections, etc., contains the results of GREW's earlier and later studies. It is to this work that the following page citations refer. GREW and his contemporary MALPIGHI were the first to place the study of plant anatomy upon a scientific basis.

GREW's treatment of plant physiology in the four main books of his volume is largely chemical while the seven supplementary lectures (see references) upon mixtures, menstrua, salts, colors, tastes, odors, and solution of salts are entirely so. GREW's method of presentation is purely mechanistic, as indicated in his dedication of the work to King CHARLES II, the patron of the Royal Society.

"The ascent of the Sap, the Distribution of the Aer, the Confection of several sorts of Liquors, as Lymphas, Milks, Oyls, Balsames; with other parts of Vegetation, are all contrived and brought about in a Mechanical Way. In sum, Your Majesty will find, that we are come ashore into a new World, whereof we see no end."

Following the ancient quarternary doctrine GREW recognizes four external factors which contribute to the growth of plants — "Earth, Water, Aer and Sun" (p. 21). Of earths or soils there are several kinds, as Mellow, Sandy, Clayie, Chalky, etc., and mixtures of the same. The simple soils are of mineral, vegetable or animal origin and experiments upon the growth of plants should be conducted on single soils of the different types "that it may appear how far any of these may contribute to the growth of a plant; or to one above another." The constituent principles of soils are to be examined by the chemical processes of distillation, calcination, etc.

Of waters, GREW recognized also various kinds as Rain, Well, Spring, River, Snow, Sea, etc. He suggested experiments upon the growth of plants in each type of water and in other liquids as urine, milk, whey, wine, etc., and also of solutions of different substances in these fluids, as salt, niter, sal prunella, soap, etc. GREW, like other investigators of his time, followed the "drag-net" method of experimentation pursued by BACON.

In his dedication to CHARLES II, GREW states that "a Plant lives partly upon Aer, for the reception whereof, it hath those Parts which are answerable to Lungs." He mentions that the air may be "impregnated with vegetable principles" and that it may contain a "true Aerial Salt . . . dissolved in the Aether, as other Salts are in Water, or in the Vaporous parts of the Aer" (pp. 22-3).

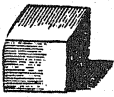
In enumerating Sun as the fourth factor essential for plant growth, instead of fire, GREW seemed to have a dim recognition of other solar influences besides heat, but his ideas upon this subject were too nebulous for the construction of any theory resembling that of photosynthesis.

In developing his notions of plant nutrition GREW regarded the root as the mouth through which the watery solution of nutriments entered along with air, from the soil. He held that the oil and all other principles of plant growth existed preformed in this aqueous fluid, a conception some-

Tab. LIII

Marine Salt

f¹



Nitrous

2.



Alkaline

3



Acid

4

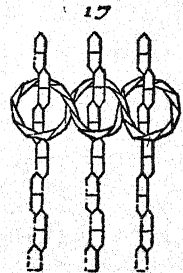
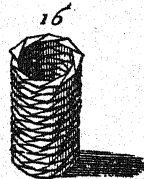
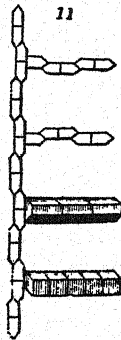
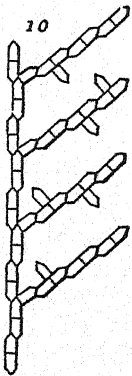
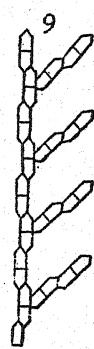
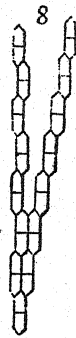
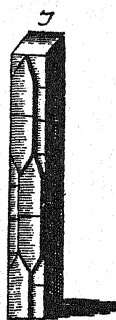
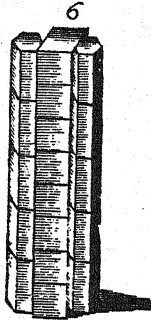
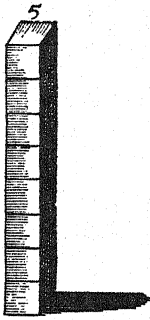
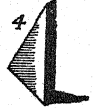


FIG. 16. — Grew's representation of how chain-like combinations of the crystals of different salts may form the skeletons of plant structures. — Illustration from GREW's "Anatomy of Plants", 1682, Plate LIII.

what analogous to the ancient homoeomeric doctrine of the Greek philosopher ANAXAGORAS.

"If it be asked, how a Plant comes to have any Oyl at all in any Part? Since we see, that the Sap by which the Root is fed, seemeth to be nothing else but Water: and that many Plants which yield a great deal of stillatitious Oyl, as Mint, Rue, and others, will yet grow in Water: I say, if it be enquired how this Water is made Wine or Oyl? I answer, that there is no such matter. But that the Oyl, and all other Vegetable Principles are actually existent in, and mixed per minima, though in an extraordinary small proportion, with the Water. Even as we see the distilled Waters of Anise Seeds, Penyroyal, and the like to be impregnated with their own Oyls, which give the Taste and Smell to such Waters.

"Wherefore, as a certain quantity of any Salt may be dissolved in Water; beyond which, it will not mix therewith, but remains under its own Form: So is there a certain proportion of Oyl, though far less, which may also be perfectly mixed with Water; and is certainly so, more or less, with all the Water in the World. But if that proportion, or degree of impregnation be once exceeded; the particles of Oyl do then, and not till then, gather into a body, and appear under their own Form.

"I say therefore, that all kinds of Vegetable Principles, are either in or together with the Water, with less difference first received into a Plant. But when they are once therein; they are then separated, that is to say, filtered, some from others, in very different Proportions and Conjunctions by the several Parts; the Watery by one Part, the Aery by another, the Oily by another, and so the rest: and so every Part is the Receptacle of a Liquor, become peculiar, not by any Transformation, but only the Percolation of Parts out of the common Mass or Stock of Sap. And so all those parts of the Sap, which are superfluous to any kind of Plant, are at the same time, discharged back by Perspirations, into the Aer" (pp. 132-3).

The nutritive soil solution, according to GREW, underwent processes of fermentation, concoction, separation and filtration in the root, after which it passed through the stem to the leaves whence after further elaboration it flowed to the fruit, seed and other organs where its salts, oils, etc., were coagulated and fixed into the substance of the plant. In this process of fixation GREW conceived the saline constituents of the sap to be the chief governing principles,

"whether Alkaline, Acid, or of any other Kind; being in some sort as the Mold of a Button, to which the other Principles, as its Attire, do all conform. Or the Salts are, as it were, the Bones; the other Principles, as the Flesh which covers them" (p. 158).

In plate 53 of his book GREW gives in fact crystallographic representations of marine, nitrous, alkaline, and acid salts and shows by fanciful drawings how the chain-like combination of these elemental forms may constitute the skeleton of plant structures. This fantastic mechanical conception is carried even to the point of supposing that the peculiar fibrous or spiral or hollow structure of different plant tissues is governed this way:

"By mediation of their Principles the Parenchymous Parts likewise of a Root have their proper contexture. For from their Acid Salt they are Fibrous; from their Oyl, the Fibres are Round and in all parts even within themselves; and from their Spirit, it is most probable, that they are also hollow. But because the Spirit is, here, more copious than the Aer; and the Saline Principle an Acid, and so, more under the government of the Spirit, than is an Alkali; therefore are not the said Fibres continued in straight Lines, as the Sap-Vessels; or by one uniform motion, into spiral lines, as the Fibres in the Aerial; but winding, in a circular manner, to and fro a thousand ways, agreeable to the like motions of the Spirit, that most active and here most predominant Principle" (p. 87).

A similar explanation was given for the change in composition of fer-

menting liquors by the growth of micro-organisms, which GREW, with acute vision, regarded as of a vegetable nature.

"A further Argument hereof may be deduced from the Cuticular and other Concretions, commonly called Mothers, in Distill'd Waters, Vinegar and other Liquors. For in these Concretions, there is always a tendence to Vegetation; and many of them are true Vegetables in their Kind; as shall hereafter be seen. Now the Liquors, in which these are generated, do always, wholly or in part, lose their Taste and Smell, and so become Vapid. The more sensible Principles therein having made their Transit from the Fluid, into the Concrete Parts. So, I have known, sometimes, Vinegar it self, to become by these Concretions, almost as Tasteless as Common Water. Whereby it seems evident, That of Vegetable Principles, there are some more Masterly than others: and that of these, the Saline is the chief. The same is likewise argued from the frequent Experiment of many good Husband-men; that most Bodies which abound with Salt, are the greatest Nourishers of Plants" (p. 158).

The passage cited is an interesting example of an early effort to explain how "vinegar in time will eat itself up", to employ a homely phrase of modern rustic origin.

GREW, like some writers of recent times, had unbounded faith in the capacity of the chemist to duplicate the operations of nature. "We may not only imitate Nature," he exclaims, "but in some cases go beyond her" (p. 231). His instances of how the operations of nature can be duplicated in the laboratory are pleasing illustrations of the sublime confidence which was had in the possibilities of chemistry at the very birth of the science. This is shown in GREW's description and explanation of what is now known as the elaidin reaction of olive oil.

"First, For the Imitation of an Animal Body, I will instance in Fat. Which may be made thus; Take Oyl Olive, and pour it upon high Spirit of Nitre. Then digest them for some days. By degrees, the Oyl becomes of the colour of Marrow; and at last, is congealed, or hardned into a white Fat or Butter, which dissolveth only by the fire, as that of Animals. In converting Oyl thus into Fat, it is to be noted, That it hardens most upon the exhalation of some of the more Sulphureous parts of the Spirit of Nitre. Which I effected, well enough for my purpose, by unstopping the glass after some time of digestion; and so suffering the Oyl to dissolve and thicken divers times by successive heat and cold. Hence, The true Congealing Principle, is a Spirit of Nitre separated from its Sulphur. For the better doing whereof, the Aer is a most commodious Menstruum to the said Spirit of Nitre. Whence also, if we could procure such a Spirit of Nitre, we might congeal Water in the midst of Summer. We might also refrigerate Rooms herewith Artificially. And might Imitate all frosty Meteors. For the making of Fat, is but the Durable Congelation of Oyl: which may be done without frost, as I have shewed how.

"Hence also it appears, That Animal Fat it self, is but the Curdling of the Oily parts of the Blood; either by some of its own Saline parts; or by the Nitrous parts of the Aer mingled therewith" (p. 233).

GREW recognized three classes of salts in plants, (1) the mineral or marine salts such as common salt, (2) the essential salts such as occur naturally in plants as tartar, and (3) the lixivial or alkaline salts which constitute the ash of plants and plant products. His "Essay of the Various Proportions wherein the Lixivial Salt is found in Plants" is of great interest to agricultural chemists as it contains some of the earliest published examples of quantitative ash determinations, although the more extensive analyses of REDI were made at an earlier date. GREW employed in his weighings a pound which consisted of 16 ounces = 128 drams = 384 scruples = 7680 grains. A few determinations are quoted:—

"Of Marjorane, which is Aromatick, one pound affords but one Scruple of Lixivial Salt: which is but the 384th part of the whole pound."

"Of Mint, which is Hot and Bitter, one pound yields 5 Drachms and a Scruple or the 24th part."

"Of Sea Scurvygrass, which is Salt, one pound yields 9 Drachms and a Scruple or 28 Scruples; which is near the 13th part of the whole. A greater proportion of Salt, than in any other Plant upon which I have hitherto made Tryal: or even in Tartar it self. Yet it is not a Marine, but true Lixivial Salt: as is evident; both from its Taste; and in that it maketh an Effervescence with Spirit of Salt (i. e. hydrochloric acid); which Sea-Salt will not do."

"Jalap (one pound) yields but one Drachm and 15 Grains, or 102^d part" (pp. 256-7).

The calculated percentages of Lixivial Salt or water soluble ash in the above cases varied from 0.26 for Marjoram to 7.29 for Sea Scurvygrass. GREW recognized the variable quantity and character of the ashy residues which he obtained from different plants and remarked, "that there are divers kinds of Earths, even in Plants, of which, as well as of Salts, etc., some are volatile." GREW made attempts, as did REDT, to isolate different salts from his ashy residues by fractional crystallization of the aqueous solutions but the art of chemical analysis was not sufficiently advanced to enable him to proceed very far in this difficult direction. He could only conclude,

"that a Lixivial Salt is not only a compounded Body of Salt, Sulphur, Aer and Earth; but even a Compounded Salt, containing both a Vegetable Nitre, and a true Sea Salt. Secondly, that the Exposing of Bodies, in the manner above shewed, may justly be accounted one Part of Chymistry hitherto Deficient, and much farther to be improved for the Discovery of the Nature of Bodies" (p. 267).

GREW was a pioneer also in the study of vegetable colors. In his "Discourse of the Colours of Plants" read before the Royal Society in May 1677, he described a large number of tests upon the changes produced in the colors of plants by different chemicals, as acids, alkalies, salts, etc. Some of these experiments might be described as early pH studies with plant indicators. A few of GREW's conclusions upon the subject are quoted:—

"As Alkalys, or other Analogous Salts, are predominant in Greens, so Acids in Reds, especially in the brighter Reds, in the Leavs and Flowers of Plants. Hence it is, that Spirit of Nitre dropped upon the Blew Flower of Ladies Looking-Glass, Larkspur, Borage, turns them all Red, sc. into the Red of Common Lychnis. But (which is particularly to be noted) being dropped on the said Red Flowers of Lychnis, alters them little or nothing; because, that very colour is therein produced by a copious admixture of the like Principle.

"The Summ therefore of what hath now been said, of the causes of Vegetable Colours, is this: That while their Sulphur and Saline Principles, only swim together, and are not as yet united into one Precipitate, no Colour results from them, but the Contents are rather Limpid; as usually in the Root, and many other Parenchymous Parts.

"When they are united, and the Alkaline are predominant, they produce a Green.

"When the Sulphur and the Alkaline are more equal, they produce a Tauny.

"When the Sulphur, Acid and Alkaline, there a Yellow.

"When the Sulphur predominant, and the Acid and Alkaline equal, there a Blew.

"When the Sulphur and Acid are predominant to the Alkaline, then a Purple.

"When the Sulphur predominant to the Alkaline and the Acid to them both, a Scarlet.

"Lastly, When the Acid predominant to the Alkaline, and the Sulphur to them both, a Blood-Red; which is the highest and most Sulphurious Colour in Nature" (pp. 276-7).

As a general deduction from his experiments GREW suggests that the prevailing green color of vegetation may result from the action of "some Alkaline or other like Salt in the Aer."

Another factor in determining the color of plants, according to GREW, is the soil whose influence in this respect he thought might be modified by the addition of various salts. GREW's suggestion, which has been followed in modern times by florists for changing the tints of hydrangeas and other flowers, is as follows :—

"The consideration whereof, and of the foregoing Experiments, may direct us not only in changing the Bed, but also in compounding the Soyl, as by mixing such and such Salts, or Bodies impregnated with such Salts, I say by mixing these Bodies in such a proportion, with the Soyl, as although they have no Colour in themselves, yet may be effectual to produce a great variety of Colours in the Plants they nourish; supplying the Plants with such Tinctures, as shall concur with the Aer, to strike or precipitate their Sulphur into so many several Colours, after the manner above explicated: and so to bring even Natures Art of Painting, in a great part, into our own power" (p. 278).

GREW was a follower of the atomic philosophy of DEMOCRITUS in his explanation of taste. He recognized no less than sixteen simple flavors — bitter, sweet, sour, salty, hot, cold, aromatic, nauseous, astringent, pungent, penetrant, stupifacient, continual, intermittent, still, and tremulous — of which he differentiates and tabulates a vast number of combinations. His classification is an interesting early attempt to solve a still unsettled problem. His explanation of the causes of tastes is quoted in part :—

"The immediate Causes, besides the Organs of Taste, are the Principles of Plants. As many of which, as come under the notice of Sense, we have already supposed to be these Seven, Alkali, Acid, Aer, Water, Oyl, Spirit and Earth. The Particles both of Alkaline and Acid Salts, are all angular and poynted. Those of Aer, properly and strictly so called, are Elastick or Springy; and therefore also Crooked; as I have likewise formerly conjectured. And I find the Learned Borelli, in a book of his since then published, to be of the same Opinion. Those of all Fluid Bodies, quâ Fluid, and therefore of Water, Oyl and Spirit, I conceive to be Globular, but hollow, and with holes in their Sides. Those of Water, to be larger Globes, with more holes; those of Oyl, to be lesser, with fewer holes; and those of Spirit the least. Lastly, that the particles of Earth are also Round; yet angular; and nearer to a solid.

"These Principles affect the Organs of Sense, according to the variety of their Figures, and of their Mixture. So those which are sharp or poynted; and those which are springy; are fitted to produce any stronger Taste: and those which are round, are apt, of their own Nature, to produce a weaker or softer one. And so by the diversities of their Mixture; not only with respect to their Proportion, but also the very Mode of their Conjunction. Hence it is, that many Bodies which abound with Salt, as Ambar with an Acid, and the Bones of Land-Animals with an Alkaline, have notwithstanding but a weak Tast; the Saline Parts being in the former drowned in the Oyl, and in the latter also buried in the Earth" (p. 286).

Space is lacking to quote further from NEHEMIAH GREW's "Anatomy of Plants". The botanical title of this work has caused it to be overlooked by historians of chemistry and this is unfortunate for the book is replete with observations that have a bearing upon many modern applications of this science. GREW's treatise was a bold effort to supplant the superstition and mysticism of earlier writers with purely mechanistic conceptions. While his explanations are often crude and imperfect, his method exemplified perfectly the new praiseworthy departure that characterized the work of

the early members of the Royal Society who could truly say, "We are come ashore into a new World, whereof we see no end."

REFERENCES:—

- GREW, NEHEMIAH (1672): *The Anatomy of Vegetables begun. With a general Account of Vegetation founded thereon.* London, S. Hickman.
- (1682): *The Anatomy of Plants with an Idea of a Philosophical History of Plants and several other Lectures read before the Royal Society.* London.
References to Grew's Lectures Before the Royal Society
Published in His Anatomy of Plants:—
- I. The Nature, Causes, and Power of Mixture. Dec. 10, 1674; pp. 221-37.
 - II. The Luctation arising from the Affusion of several Menstruums upon all sorts of Bodies. April 13 and June 1, 1676; pp. 238-54.
 - III. Various Proportions wherein the Lixivial Salt is found in Plants. March, 1676; pp. 255-60.
 - IV. The Essential and Marine Salts of Plants. Dec. 21, 1676; pp. 261-8.
 - V. The Colours of Plants. May 3, 1677; pp. 269-78.
 - VI. The Diversities and Causes of Tasts; chiefly in Plants. With an Appendix, of the Odours of Plants. March 25, 1675; pp. 279-93.
 - VII. The Solution of Salts in Water. Jan. 18, 1677; pp. 296-304.

John Winthrop, the Younger (1606-1676):—The early "Philosophical Transactions" of the Royal Society contain several articles of agricultural chemical interest. The first of these to be mentioned is by the younger WINTHROP, who, emigrating to New England in 1631, was most active in promoting its agricultural and chemical resources. As Governor of Connecticut he sailed for England in 1661 to obtain a Royal Charter for this colony and during his absence he became a member of the Royal Society to which he contributed various papers and reports. His paper "Of the Manner of Making Tar and Pitch in New England," presented in July 1662, is the first contribution by an American before a scientific society. In January 1663, WINTHROP was requested by the Royal Society to undertake an experiment upon the brewing of beer from maize and his report upon this subject was afterwards included in a paper upon the "Description, Culture and Use of Maize" from which the following extract is quoted:—

"The Stalk groweth to the hight of 6. or 8. feet; more or less, according to the condition of the Ground, or kind of Seed. . . . 'Tis always joynted like a Cane. And is full of sweet juice, like the Sugar-Cane. And a Syrup as sweet as Sugar may be made of it; as hath been often try'd. And Meats sweetned with it, have not been distinguished from the like sweetned with Sugar. Trial may easily be made, whether it will not be brought to Crystallize or shoot into a Saccharine Powder, as the juice of the Sugar-Cane

"Before they had Mills, having first watered and Husked the Corn, and then beaten it in Wooden Mortars; the courser part sifted from the Meal, and separated from the loose Hulls by the Wind, they boyled to a thick Batter: to which being cold, they added so much of the fine Meal, as would serve to stiffen it into Past, whereof they made very good bread

"The English have also found out a way to make very good Beer of Grain: that is, either of Bread made hereof, or else by Malting it. The way of making Beer of Bread, is by breaking or cutting it into great lumps about as big as a mans fist, to be mash'd, and so proceeded with as Malt, and the impregnated Liquor, or Woort, either adding or omitting Hopps, as is desired."

"To make good Malt of this Corn, a particular way must be taken. The Barly-Malt-Masters have used all their skill to make good Malt hereof the ordinary way; but cannot effect it; that is, that the whole Grain be Malted, and tender and flowry, as in other Malt. For it is found by experience, that this Corn, before it be fully Malted, must sprout out both ways, (i. e. both Root and Blade) to a great length;

of a finger at least; if more, the better. For which, it must be laid upon an heap a convenient time. Wherein on the one hand, if it lyeth of a sufficient thickness for coming, it will quickly heat and mould, and the tender Sprouts be so intangled, that the least opening of the Heap breaks them off; and so hinders the further maturation of the Grain into Malt. On the other, if it be stirred and opened to prevent too much heating, these sprouts which have begun to shoot, cease growing, and consequently the Corn again ceaseth to be promoted to the mellowness of Malt.

"To avoid all these difficulties, this way was try'd and found effectual. Take away the top of the Earth in a Garden or Field two or three inches, throwing it up half one way, and half the other. Then lay the Corn, for Malt, all over the Ground so as to cover it. Then cover the Corn with the Earth that was pared off: and there is no more to do, till you see all the Plot of Ground like a green Field covered over with the Sprouts of the Corn, which will be within ten days or a fortnight, according to the time of the year. Then take it up, and shake the earth from it and dry it. For the Roots will be so intangled together, that it may be raised up in great pieces. To make it very clean, it may be washed, and then presently dry'd on a kiln, or in the Sun, or spread thin on a Chamber floor. This way, every Grain that is good will grow, and be mellow, flowry, and very sweet; and the Beer made of it, be wholsom, pleasant, and of good brown colour.

"Yet Beer made of the Bread, as aforesaid, being as well coloured, as wholsom and pleasant, and more durable; this therefore is most in use. And the rather, because the way of Malting this Corn, last described, is as yet but little known amongst them" (Phil. Trans. XII, pp. 1065-9).

WINTHROP can be called the earliest agricultural and industrial chemist of the New World. He established a laboratory for the examination of colonial products, collected a large chemical library, and among many other activities founded a stock company for manufacturing saltpeter from the excreta of farm animals.

REFERENCE:—

WINTHROP, JOHN (1683): Description, Culture and Use of Maize. Philosophical Transactions of The Royal Society, London, Vol. XII.

John Clayton* (latter half of 17th century):—Reports to the Royal Society, similar to those made by WINTHROP for New England, were made later for the colony of Virginia by JOHN CLAYTON, who was Rector of Crofton at Wakefield in Yorkshire and transmitted to the Royal Society in May 1688 an account of the scientific observations which he made during a residence in Virginia between 1684 and 1686. His report, in Vol. 17 (1693) of the Philosophical Transactions of the Royal Society, from which the following extracts are taken, gives a graphic picture of the theories and practices of agricultural chemistry which prevailed at that time. The references made by CLAYTON to the production of coal gas (the earliest recorded), spontaneous combustion, use of indicators, chemical examination of water, soil, and tobacco; and the employment of animal manure, marl, lime, and humus, as fertilizers have also a great historic interest. The parts of CLAYTON's letter relating to the waters, soils, and fertilizer resources of early Virginia and the effect of different soils on the quality of tobacco constitute the first detailed agricultural chemical report in the history of colonial America.

* This JOHN CLAYTON is not to be confused with his later namesake, the colonial botanist of Virginia.

"An Account of Several Observables in Virginia"

"Having oftentimes been urged to give an account of Virginia, by several of the Worthy Members of the Royal Society, I cannot but, as far forth as I am able, obey commands whereby I'm so much honour'd and show my respect by my ready compliance; tho' I am so sensible of my own weakness and incapacity to answer your expectations, that before hand I must apologize for myself. And indeed by sea I lost all my Books, Chymical Instruments, Glasses and Microscopes, which rendered me incapable of making those Remarks and Observations I had designed, they were all cast away in Captain Wins Ship, as they were to follow me; and Virginia being a Country where one cannot furnish ones self again with such things, I was discouraged from making so diligent a Scruteny as otherwise I might have done . . ." (*loc. cit.*, p. 781).

"Of the Air"

"I have been told by very serious Planters that 30 or 40 years since, when the Country was not so open, the Thunder was more fierce and that sometimes after violent Thunder and Rain, the Roads would seem to have perfect casts of Brimstone; and 'tis frequent after much Thunder and Lightning for the Air to have a perfect Sulphureous Smell. Durst I offer my weak Reasons when I write so Great Masters thereof, I should here consider the nature of Thunder, and compare it with some Sulphureous [i. e. combustible] Spirits which I have drawn from Coals, that I could no way condense, yet were inflammable; nay, would burn after they pass'd through Water, and that seemingly fiercer, if they were not over-power'd therewith. I have kept of this Spirit a considerable time in Bladders; and tho' it appeared as if they were only blown with Air, yet if I let it forth, and fired it with a Match or Candle, it would continue burning till all were spent. It might be worthy Consideration likewise, whether those frequent Thunders proceeded from the Air's being more stagnant, the Motion of the Winds being impeded by the Trees, or whether the Motion of the Winds being obstructed by them below, the Motion might not be more violent aloft; and how far that may promote Inflammability; for Stacks of Hay or Corn that ferment with Moisture, never burn, unless when brisk Winds blow, that agitate and fan the little fermenting Sparks, and oft kindle them into an actual Fire" (*loc. cit.*, pp. 788-9).

"Of the Water"

"As for the Waters in the Springs in general, they are, I think, somewhat more eager than those in England. In that I have observed, they require some quantity more of Mault to make strong Beer than our English Waters and will not bear Soap. I have try'd several by infusing of Galls and found little difference in the Colours, turning much what the Colour of common Sack in Taverns. I tried two wells at Colonel Bird's by the Falls of James River, several Wells near James Town, some Springs in the Isle of Wight County: There's a Spring in the Isle of Wight, or Nanzamond County, vents the greatest Source of Water I ever saw, excepting Holy Well in Wales, but I had not opportunity to make experiments thereof. I tried likewise some Springs on the banks of York River, in New Kent and Gloucester County, but found them vary very little as to Colour. I could not try anything as to their specifick Gravity, having neither Aquapoise, nor those other Glasses I had contrived pecuniary for making such Experiments, they being all lost with my other things. I had Glasses blown would hold about Five Ounces, others about Ten Ounces, with necks so small, that a Drop would make a considerable Variation; with these I could make much more critical and satisfactory observations as to the specifical Gravity of Liquors, having Critical Scales, than by other way yet by me tried . . ." (*loc. cit.*, pp. 793-4).

"Of the Earth and Soil"

"The soyl in general is sandy: I had designed, and I think it might be worth a Critical Remark, to observe, the Difference of Soyls seem appropriated to the several sorts of Tobacco: for there is not only the two distinct sorts of a Sweet-scented and Aranoko tobacco; but of each of these be several sorts much different, the Seeds whereof are known by distinct Names, they having given them the Names of those Gentlemen most famed for such sort of Tobacco, as of Prior-seed, etc. Nay, the same sort of seed in different Earths, will produce Tobacco much different, as to goodness. The richer the Ground, the better it is for Aranoko tobacco, whose Scent is not much

minded, their only aim being to have it specious, large, and to procure it a bright Kite's-foot colour. Had not my Microscopes, etc. Tools to grind Glasses, been cast away, with my other things, I had made some Critical Enquiries into their several Natures, I would have examined what Proportions of Salts, all the sorts of Earths had afforded, and how Water impregnated with their Salts, would have changed with infusing Galls, how with the Syrup of Violets and how they would have precipitated Mercury, or the like, and so far forth as I had been able, examined them by the several Tryals of Fire. I conceive Tobacco to be a plant abounding with Nitro-sulphurous Particles; for the Planters try the goodness of their Seed, by casting a little thereof into the Fire; if it be good, it will sparkle after the manner of Gunpowder: so will the Stalks of Tobacco-leaves and perhaps has something analagous to the Narcotick Sulphur of Venus, which the Chymists so industriously labour after. The World knows little of the efficacy of its Oyl, which has wonderful Effects in the curing of old inveterate Sores and Scrophulous Swellings, and some otherwise applied and qualified. The goodness of Tobacco I look on primarily consists in the volatility of its Nitre: And hence the sandy Grounds that are most impregnated therewith, and whose Nitrous Salt is most volatile, for such Grounds are quickest spent, yield Tobacco's that have the richest Scent and that shortly become a pleasant Smoak; whereas, in Tobacco that grows on stiff Ground, the Salts seem more fix'd, and lock'd up in the Oyl, so that whilst new, 'tis very heady and strong, and requires sometime for its Salts to free themselves, and become volatile; which it manifests by its having an Urinous Smell. The same Reason satisfies, why Tobacco that grows on low Lands as far as the Salts, tho' the Plant be never overflowed with Salt Water, yet the Ground that feeds the Plant being impregnated with Salt Water, that Tobacco smoaks not pleasantly, and will scarcely keep Fire, but do all that a Man can, will oft go out, and gives much trouble in frequent lighting the Pipe, 'till after it has been kept some considerable time: which may be assign'd to the more fixed Saline Particles of the Marine Salt in these Plants, which require more time ere they be render'd volatile. Here it might be worthy an Enquiry into the Nature of Filtration of Plants, since we may hence gather, Particles of the Marine Salt are carried along with the *Succus Nutritius* of the Plant; concerning which, if it were not too much to deviate from the Matter in hand, I should offer some Reflections of my own, which the Learned Society might perhaps improve: for I think thence might be made many happy Conjectures as to the Virtues of Plants. So where we see Plants, or Trees of an open Pore growing low, we shall find their Juice has subtle parts; So have all Vines, whether the Grape Vine, or Briony, or a Smilax or the like. If a Gummosus Plant or Tree that grows low and close pored, it abounds with acid Spirits, as *Lignum vitæ*, etc. if it grow tall and be open pored, it abounds with a subtle volatile Spirit, as your Firss and the Turpentine Tree. But to insist no further herein, than as this may be applicable to the present Discourse: for I have observed, that that which is called Pine-Wood Land, tho' it be a sandy Soyl, even the Sweet-scented Tobacco that grows thereon, is large and porous, agreeable to Aranoko tobacco; it smoaks as coarsly as Aranoko: wherefore 'tis, that I believe the Microscope might make notable Discoveries towards the knowledge of good Tobacco: for the closer the Composition of the Leaf, the better the Tobacco; and therefore the Planters and Merchants brag of the Substance of their Tobacco; which word, did they always take it in a true sense, for the Solidness and not mistake it for the thickness, it would be more consonant to a true Observation: for as I said of the Pine-wood Tobacco, some of it is thick and not solid, and differs from the best tobacco as Buff does from tann'd Leather: so that if the Tobacco be sound and not rotten, you may give a great guess at the goodness of Tobacco, when you weigh the Hogsheds, before you see them: for if an equal care be taken in the Packing of them, the best tobacco will weigh the heaviest, and pack the closest. Now I said, that the Sweet-scented Tobacco most in vogue, which was most famed for its scent, was that that grew on sandy Land; which is true, if you would smoak it whilst new, or whilst only two or three Years old; but if you keep the stiff Land Tobacco, which is generally a Tobacco of great Substance five or six Years, it will much excel: for tho' the sandy Land Tobacco abound with a volatile Nitre at first, yet the stiff Land Tobacco abounds with a greater quantity of Nitre, only that it is locked up in its Oyl at first, and requires more time to extricate itself, and become

volatile; but the Pine-wood Land having little of the Nitro-Sulphurous Particles, neither is, nor ever will make anything of a rich Smoak" (*loc. cit.*, pp. 943-6).

"But now to return to the Reflections of Improving, and Manuring of Land in Virginia; hitherto, as I have said, they have used none but that of Cow-penning; yet I suppose they might find very good Marle in many places,—I have seen both the red and blew Marle at some breaks of Hills: This would be the properest Manure for their Sandy Land, if they spread it not too thick, theirs being, as I have said, a shallow Sandy Soil, which was the Reason I never advised any to use Lime, tho' they have very good lime of Oyster shels; but that's the properest Manure for cold Clay Land, and not for a Sandy Soil. But as most Lands have one Swamp or another bordering on them, they may certainly get admirable Slitch [*i. e.* muck], wherewith to Manure all their uplands. But this, say they, will not improve Ground, but clods and grows hard; 'tis true, it will do so for some time, a Year or two at the first; but did they cast it in heaps, and let it lye for two or three Years after a Frost or two had seized it, and it had been well pierced therewith, I doubt not it would turn to good account: And for this too I have something more than bare conjecture; for Discoursing it once with a good notable Planter, we went to view a heap thereof, that casually he had cast up 'twixt three and four Years before, and we found it not very binding, but rather a fine Natural Mold, whereupon he did confess, he then remembered that out of a ridge of the like Mold he had very large Plants, which must have been of the like Slime or Slitch cast up before: But said, that himself and others despaired of this Manure because they had taken of this Slitch fresh and moist out of the Swamp and fill'd Tobacco Hills with it, and in the midst of it planted their Plants, which so bound the Roots of their Plants, that they never came to anything" (*loc. cit.*, pp. 984-5).

REFERENCE:—

CLAYTON, JOHN (1693): An Account of Several Observables in Virginia. Philosophical Transactions of the Royal Society, London, Vol. 17.

John Woodward (1665-1728):—The next quotation from Vol. 21 (1699) of the early Philosophical Transactions of the Royal Society is of great historic importance as it supplied for the first time experimental evidence against the supposition of VAN HELMONT and BOYLE that water is the parent material from which the substance of plants is derived. The contribution entitled, "Some Thoughts and Experiments Concerning Vegetation" (pp. 193-227) is by Dr. JOHN WOODWARD of the College of Physicians and Professor of Medicine in Gresham College, London.

"The great restorer of Philosophy in this last Age, my Lord BACON, is of opinion, 'that for Nourishment of Vegetables the water is almost all in all; and that the Earth doth but keep the Plant upright, and save it from over heat, and over cold' (Nat. Hist. Cent. 5, § 411). Others there are who are still more express; and assert Water to be the only Principle or Ingredient of all natural things. They suppose that, by I cannot tell what Process of Nature, Water is transmuted into stones, into plants and, in brief, all other Substances whatever. HELMONT (Complexionum atque Mistionum Element. Figm.) particularly and his Followers are very positive in this; and offer some experiments to render it credible. Nay a very extraordinary Person of our own Nation (BOYLE, Scept. Chem., par. 2) tries these experiments over again; and discovers a great Propensity to the same thoughts and opinion they had: declaring for this Transmutation of Water into Plants and other Bodies, tho' with great Modesty and Deference, which was his usual manner" (pp. 193-4).

"Vegetables are not form'd of water: but of a certain peculiar terrestrial matter. It hath been shewn that there is a considerable quantity of this matter contain'd both in rain, spring and river water: that the much greatest part of the fluid mass that ascends up into plants does not settle or abide there, but passes through the pores of them and exhales up into the Atmosphere; that a great part of the terrestrial matter, mixt with the water, passes up into the plant along with it; and that the plant is more or less augmented in proportion as the water contains a greater or smaller quantity of that

matter. From all which we may very reasonably infer, that Earth, and not Water, is the matter that constitutes vegetables" (pp. 218-9).

Many experiments are described by WOODWARD to prove his argument. The following results were obtained in 1692 with mint when allowed to grow 56 days in distilled water, in Hyde Park water, and in Hyde Park water shaken with $1\frac{1}{2}$ ounces of garden earth:—

KIND OF WATER	WEIGHT OF PLANT		GAIN IN WEIGHT	WEIGHT WATER TRANSPIRED	RATIO OF GAIN TO WATER TRANSPIRED
	AT BEGINNING	AFTER 56 DAYS			
	<i>Grains</i>	<i>Grains</i>	<i>Grains</i>	<i>Grains</i>	
Distilled	114	155	41	8803	1:214 ²⁵ / ₄₁
Hyde Park	110	249	139	13140	1:94 ⁷⁴ / ₁₃₉
Hyde Park shaken with earth	92	376	284	14950	1:52 ⁹¹ / ₁₄₂

The gain in weight is not proportional to the amount of water transpired, as one would expect if the hypothesis of VAN HELMONT and BOYLE were true, but to the amount of mineral matter dissolved in the water.

The following practical inferences are then drawn by WOODWARD as a result of his experiments:

"Why . . . I limit the proportion of the Augment of the plant to the quantity of proper terrestrial matter in the Water is because all, even the Vegetable Matter, to say nothing of the mineral, is not proper for the nourishment of every plant. There may be, and doubtless are, some parts in different species of plants, that may be much alike and so owe their supply to the same common matter; but 'tis plain all cannot. And there are other parts so differing, that 'tis no way credible they should be form'd all out of the same sort of corpuscles. So far from it, that there want not good indications . . . that every kind of vegetable requires a peculiar and specifick matter for its formation and nourishment. Yea, each part of the same vegetable does so; and there are very many and different ingredients go to the composition of the same individual plant. If therefore the soil, wherein any vegetable or seed is planted contains all or most of these ingredients, and those in due quantity, 'twill grow and thrive there; otherwise 'twill not. If there be not as many sorts of corpuscles, as are requisite for the constitution of the main and more essential parts of the plant, 'twill not prosper at all. If there be these, and not in sufficient plenty, 'twill starve and never arrive to its natural stature. Or if there be any the less necessary and essential Corpuscles wanting, there will be some failure in the Plant" (p. 214).

"Soil that is once proper and fit for the production of some one sort of Vegetable does not ever continue to be so. No, in tract of time it looses that property; but sooner in some lands and later in others. This is what all who are conversant in these things know very well. If wheat, for example, be sown upon a tract of land that is proper for that grain, the first crop will succeed very well; and perhaps the second, and the third, as long as the ground is in heart, as the farmers speak. But in a few years 'twill produce no more, if sowed with that corn. Some other grain indeed it may, as Barly. And after this has been sown so often that the land can bring forth no more of the same; it may afterwards yield good oats; and perhaps pease after them. At length 'twill become barren, the vegetative matter, that at first it abounded withal, being educed forth of it by those successive crops, and most of it born off. Each sort of grain takes forth that peculiar matter that is proper for its own nourishment. First the wheat draws off those particles that suit the body of that plant; the rest lying all quiet and undisturbed the while. And when the Earth has yielded up all of them, those that are proper for Barly, a different grain, remain still behind, 'till the successive crops of that

corn fetch them forth too. And so the Oats, and Pease, in their turn; 'till in fine all is carried off and the earth in great measure drain'd of that sort of matter.

"After all which, that very tract of land may be brought to produce another series of the same vegetables; but never 'till 'tis supplied with a new Fund of matter, of like sort with that it at first contained. This supply is made several ways. By the grounds lying fallow for some time, 'till the rain has pour'd down a fresh stock upon it. Or by the tiller's care in manuring of it. And for further evidence that this supply is in reality of like sort, we need only reflect a while upon those manures that are found by constant experience best to promote vegetation, and the fruitfulness of the Earth. These are chiefly either parts of vegetables, or of animals: which indeed either derive their own Nourishment immediately from Vegetable bodies, or from other animals that do so. In particular the blood, urine, and excrements of animals; shavings of horns and of hoofs; hair, wool, feathers; calcin'd shells; lees of wine and of beer; ashes of all sorts of vegetable bodies; leaves, straw, roots and stubble, turn'd into earth by plowing or otherwise, to rot and dissolve there; these I say are our best manures, and, being vegetable substances, when refunded back again into the earth, serve for the formation of other like bodies" (pp. 216-7).

REFERENCE:—

WOODWARD, JOHN (1699): Some Thoughts and Experiments Concerning Vegetation, The Philosophical Transactions of the Royal Society, London, Vol. 21, pp. 193-227.

Stephen Hales (1677-1761):— Another member of the Royal Society who devoted attention to the study of the atmosphere in its relation to the growth of crops was STEPHEN HALES. He was educated at Corpus Christi College of Cambridge University, England, and then entering the ministry became perpetual curate of the parish of Teddington, where in the midst of his clerical duties he found time to conduct experiments upon the growth of plants. The results of these researches were published in 1727 under the descriptive title of "Vegetable Staticks; or an Account of some Statical Experiments on the Sap of Vegetables; being an Essay towards a Natural History of Vegetation: Also a Specimen of an Attempt to Analyse the Air, by a great Variety of Chymio-Statical Experiments, which were read at several Meetings before the Royal Society." It is to the pages of this first edition that the following citations refer.

Following the early example of VAN HELMONT, HALES applied exact quantitative methods in all his experiments.

"Since we are assured," he writes in his Introduction, "that the all wise Creator has observed the most exact proportions, of *number, weight and measure*, in the make of all things; the most likely way, therefore, to get any insight into the nature of those parts of the creation, which come within our observation, must in all reason be to number, weigh and measure. And we have much encouragement to pursue this method, of searching into the nature of things, from the great success that has attended any attempts of this kind" (*loc. cit.*, pp. 1-2).

HALES' experiments were performed upon such garden vegetables as cabbages, hops, radishes, spearmint, rhubarb, parsnips, asparagus, cucumbers, pumpkins, peas, and artichokes; and upon the shrubs, vines and trees of different fruits, as currants, gooseberries, grapes, quinces, apples, pears, cherries, plums, peaches, apricots, figs, mulberries, lemons, and walnuts. He made exact measurements of the surface areas of the leaves, stalks and roots of different plants and of the amounts of water transpired from their leaves, from which he calculated the rate of movement of the sap in different

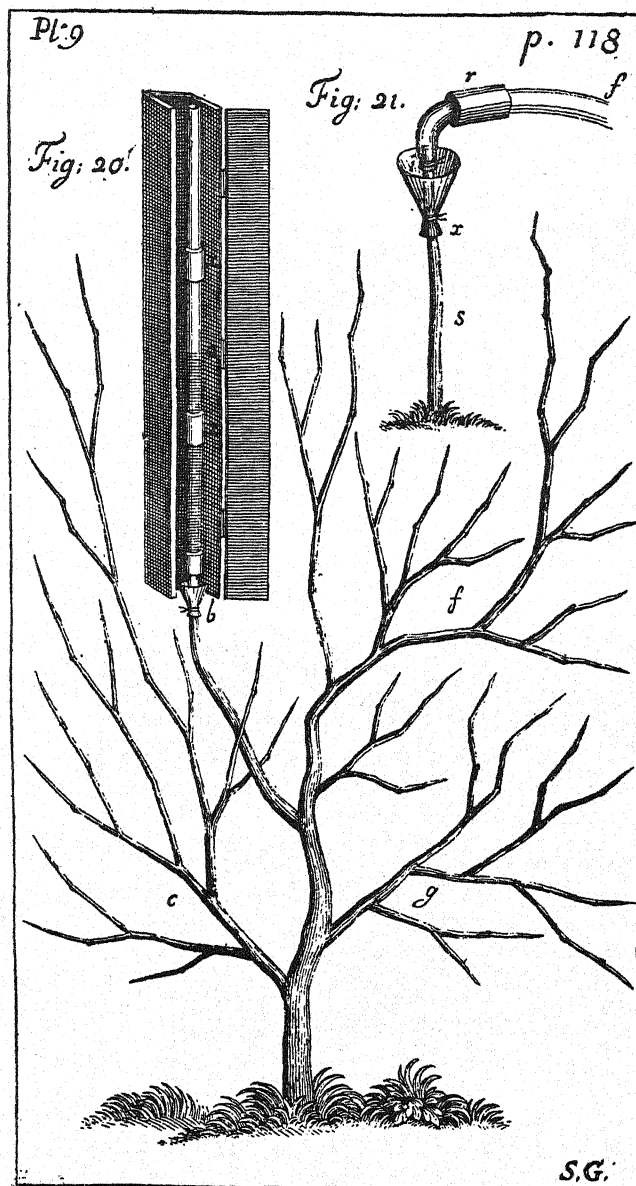


FIG. 17. — *Hale's apparatus for measuring the rise of sap in the branch of a vine.* —
 "In a prime bleeding season I fixed a tube 25 feet long to a thriving branch two years old, and two feet from the ground, where it was cut off; the sap flowed so briskly as in 2 hours to flow over the top of the tube, which was 7 feet above the top of the Vine; and doubtless would have risen higher, if I had been prepared to lengthen the tube."

tissues. The following account of one of his experiments will illustrate his method of operation:—

"From July 3d. to Aug. 3d. I weighed for nine several mornings and evenings a middle sized Cabbage plant, which grew in a garden pot, and was prepared with a leaden cover. . . . Its greatest perspiration in twelve hours day was 1 pound 9 ounces; its middle perspiration 1 pound 3 ounces, = 32 cubick inches. Its surface 2736 square inches, or 19 square feet. Whence dividing the 32 cubick inches by 2736 square inches, it will be found that a little more than the $\frac{1}{86}$ of an inch depth perspires off its surface in twelve hours day.

"The area of the middle of the Cabbage stem is $\frac{100}{156}$ of a square inch; hence the velocity of the sap in the stem, is to the velocity of the perspiring sap on the surface of the leaves, as $2736 : \frac{100}{156} :: 4268 : 1$. for $\frac{2736 \times 156}{100} = 4268$. But if an allowance is to be made for the solid parts of the stem (by which the passage is narrowed) the velocity will be proportionally increased.

"The length of all its roots 470 feet, their periphery at a medium $\frac{1}{22}$ of an inch, hence their area will be 256 square inches nearly; which being so small, in proportion to the area of the leaves, the sap must go with near eleven times the velocity thro' the surface of the roots, than it does thro' the surface of the leaves.

"And setting the roots at a medium at 12 inches long, they must occupy a hemisphere of earth two feet diameter, that is, 2.1 cubick feet of earth" (*loc. cit.*, pp. 14-6).

In the case of a sunflower HALES calculated that 17 times more fluid entered, bulk for bulk, into the sap vessels of the plant, than into the veins of a man, in 24 hours. He then remarks:—

"One reason of this greater plenty of fresh fluid in the vegetable than the animal body, may be, because the fluid which is filtrated thro' the roots immediately from the earth, is not near so full freighted with nutritive particles as the chyle which enters the lacteals of animals; which defect it was necessary to supply by the entrance of a much greater quantity of fluid.

"And the motion of the sap is thereby much accelerated, which in the heartless vegetable would otherwise be very slow; it having probably only a progressive and not a circulating motion, as in animals" (*loc. cit.*, pp. 13-4).

The experiments which HALES conducted upon the force with which trees imbibe water from the soil are classic for they were the first of their kind. Two examples are quoted. An experiment upon a grape vine in April during the "bleeding" season showed that

"the mercury was raised by the force of the sap 38 inches, equal to 43 feet $3\frac{1}{3}$ inches height of water. Which force is near five times greater than the force of the blood in the great crural artery of a horse" (*loc. cit.*, p. 107).

"In a prime bleeding season I fix'd a tube 25 feet long to a thriving branch two years old, and two feet from the ground, where it was cut off; the sap flowed so briskly, as in 2 hours to flow over the top of the tube, which was 7 feet above the top of the Vine; and doubtless would have risen higher, if I had been prepared to lengthen the tube" (*loc. cit.*, p. 117).

HALES' experiments upon the temperature of soils at different depths were also of a pioneer character. He employed 6 thermometers with stems varying from 18 inches to 4 feet in length, which he graduated by dividing the interval between the points indicated for melting ice and the highest heat of water which his hand could bear into 90 equal parts. This imperfect method of standardization is indicative of the undeveloped state of thermometry at the time. The temperatures indicated on HALES' thermometers at different depths of soil were as follows:—

DEPTH OF THERMOMETER BELOW SOIL SURFACE	TEMPERATURE BY HALES' SCALE
0 inches	48°
2 —	45°
4 —	--
8 —	--
16 —	33°
24 —	31°

HALES noted but little fluctuation in the night and day temperatures at depths of 16 and 24 inches. He attributed the penetrating power of soil moisture into the roots of plants to "the impulse of the sunbeams giving the moisture of the earth a brisk undulating motion" (*loc. cit.*, p. 64).

In his experiments upon the imbibition of water by plants HALES observed that a considerable quantity of air was also inspired from which he concluded

"It is very probable, that the air freely enters plants, not only with the principal fund of nourishment by the roots, but also through the surface of their trunks and leaves, especially at night, when they are changed from a perspiring to a strongly imbibing state" (*loc. cit.*, p. 153).

Acting upon the belief that the air inspired by plants played an important part in their nutrition HALES proceeded to make a study of the air which he supposed to be combined or fixed in various substances. Among the materials examined were wheat, peas, mustard seed, tobacco, sugar, tartar, camphor, aniseed oil, honey, bees-wax, tallow, blood, horn, oyster shells, soot, chalk, a mixture of nitre with bone-ash, and various other materials. Weighed amounts of these substances were subjected to destructive distillation in a retort and the evolved gases collected over water. The volume of gas in each case was determined and also the diminution in volume which the gas underwent on standing one or more days over water. This diminution, as in the experiment when a candle was burned over water, HALES attributed, as did MAYOW, to a loss of elasticity in the air.

Upon the basis of imperfect specific gravity determinations HALES supposed the mixture of gases which he obtained by the destructive distillation of various substances to be true air (*loc. cit.*, p. 184). But from the nature of the materials that were heated in his retorts we know that he must have produced in varying states of purity, a large number of different gases, as carbon dioxide, carbon monoxide, methane and other hydrocarbons. In case of the air distilled from peas HALES noted: —

"Nine days after this air was made, I lifted the inverted mouth of the receiver which contained it, out of the water, and put a lighted candle under it, upon which it instantly flashed; Then I immediately immersed the mouth of the receiver in the water, to extinguish the flame. This I repeated 8 or 10 times, and it as often flashed, after which it ceased, all the sulphureous spirit being burnt. It was the same with air of distilled Oyster-shell and Amber, and with new distilled air of Pease and Bees-wax. I found it the same also with another like quantity of air of Pease; notwithstanding I washed that air no less than eleven times, by pouring it so often under water, upwards, out of the containing vessel, into another inverted receiver full of water" (*loc. cit.*, pp. 171-2).

The long standing over water and repeated washing to which HALES subjected these gases removed most of the carbon dioxide and rendered the residual methane, etc., more inflammable.

HALES collected also the gas from fermenting ale, raisins, apples, sugar, wheat, barley, and peas, always under the supposition that he was dealing with air.

"That this air, which arises in such great quantities from fermenting and dissolving vegetables is true permanent air, is certain, by its continuing in the same expanded elastick state for many weeks and months; which expanding watry vapours will not do, but soon condense when cool" (*loc. cit.*, p. 203).

The air obtained by fermentation was supposed by HALES to exist in the original fruit or vegetable in a highly concentrated fixed inelastic state. An apple was found to yield on fermentation 48 times its volume of elastic "air", which caused HALES to remark that if this volume were compressed into its original space "so great an expansive force in an apple would certainly rend the substance of it with a strong explosion" (*loc. cit.*, p. 209).

In addition to his experiments upon plant and animal substances, HALES produced gases by heating sulfur, minium, sal ammoniac and other inorganic substances, by allowing aqua regia to react upon gold and antimony, nitric acid upon antimony and iron filings, oil of vitriol upon iron filings, etc., and by various other methods. He thus without knowing it generated sulfur dioxide, oxygen, hydrogen, ammonia, hydrochloric acid, chlorine, and various oxides of nitrogen. But with all this list of impending new discoveries under his hand HALES could go no farther. As RAMSAY (1896) remarks, "The prejudice in favor of the unity and identity of all these 'airs' was too great for him to overcome."

At a time when the art of chemical analysis was exceedingly undeveloped HALES' knowledge of the proximate constituents of plants was necessarily meager.

"We find by the chymical analysis of vegetables, that their substance is composed of sulphur, volatile salt, water and earth; which principles are all endued with mutually attracting powers, and also of a large portion of air, which has a wonderful property of strongly attracting in a fixt state, or of repelling in an elastick state, with a power which is superior to vast compressing forces, and it is by the infinite combinations, action and re-action of these principles, that all the operations in animal and vegetable bodies are effected.

"These active areal particles are very serviceable in carrying on the work of vegetation to its perfection and maturity. Not only in helping by their elasticity to distend each ductile part, but also by enlivening and invigorating their sap, where mixing with the other mutually attracting principles they are by gentle heat and motion set at liberty to assimilate into the nourishment of the respective parts" (*loc. cit.*, pp. 318-9).

In the application of his chemical doctrines to agriculture HALES seems to have anticipated in a way the publications of his celebrated English contemporary, JETHRO TULL, upon fine tillage. In this connection the following passage is quoted from the conclusion of the Vegetable Staticks:—

"Tho' we have from these Experiments, and from common observation, many proofs of the great expansive force, with which the fibrous roots of plants shoot, yet the less resistance these tender shoots meet with, the greater progress they will certainly make in equal times: And therefore one considerable use of fallowing and trenching

ground, and of mixing therewith several sorts of compost, as Chalk, Lime, Marle, Mold, &c. is not only thereby to replenish it with rich manure, but also to loosen and mellow the soil, not only that the air may the more easily penetrate to the roots, but also that the roots may the more readily make vigorous shoots. And the greater proportion the surface of the roots bears to the surface of the plants above ground, so much the greater quantity of nourishment they will afford, and consequently the plants will be the more vigorous, and better able to weather it out, against unkindly seasons, than those plants whose roots have made much shorter shoots. Herein therefore consists the great care and skill of the Husbandman, to adapt his different sorts of Husbandry to the very different soils, seasons and kinds of grain; that the several sorts of earth, from the very stiff and strong ground, to the loose light earths, may be wrought to the best temper they are capable of, for the kindly shooting and nourishing of the roots. And probably the Husbandman might get many useful hints, to direct him in adapting the several kinds of manure, and different sorts and seasons of culture to his different soils and grains: If in the several stages and growth of his Corn, he would not only make his observations, on what appears above ground, but would also frequently dig up, compare and examine the roots of plants of each sort, especially of those which grew in different soils, and were any how cultivated in a different manner from each other; this would inform them also, whether they sowed their Corn too thick or too thin, by comparing the branchings and extent of each root, with the space of ground allotted it to grow in.

"And since we find so great a quantity of air inspired and mixt with the sap, and wrought into the substance of vegetables, the advantage of ploughing and fallowing ground seems to arise not only from the killing the weeds, and making it more mellow, for the shooting of the roots of Corn; but it is thereby also the better exposed to having the fertilizing, sulphureous, aereal and acid particles of the air mixt with it, which make land fruitful, as is evident from the fertility which the sword or surface of land acquires, by being long exposed to the air, without any culture or manure whatever.

"We have seen many proofs of the great quantities of liquor imbibed and perspired by plants, and the very sensible influence which different states of the air had on their more or less free perspiration: A main intention therefore to be attended to in the culture of them, is to take due care, that they be sown or planted in proper seasons and soils, such as will afford them their due proportion of nourishment; which soils, as they are exhausted, must, as 'tis well known, from time to time, be replenished with fresh compost, such as is full of saline, sulphureous and aereal particles, with which common dung, lime, ashes, sword, or burn-bated turf abound: As also such manures as have nitrous and other salts in them; for tho' neither nitre nor common salt be found in vegetables; yet since they are observed to promote fertility, it is reasonable to conclude, that their texture is greatly altered in vegetation, by having their acid volatile salts separated from the attracting central air and earthy particles, and thereby making new combinations with the nutritive juice; and the probability of this is further confirmed from the great plenty of air and volatile salt, which is found in another combination of them, viz. in the Tartar of fermenting liquors: For it is the opinion of Chymists, that there is but one volatile salt in nature, out of which all other kinds of salts are formed by very different combinations, all which nutritive principles do by various combinations with the cultivated earth, compose that nutritive ductile matter, out of which the parts of vegetables are formed, and without which the watry vehicle alone cannot render a barren soil fruitful" (*loc. cit.*, pp. 363-6).

Although he was not a great discoverer, science will never let die the name of the gentle, truth-loving curate of Teddington. Meteorologists will always remember him for his work upon dew, plant physiologists will always refer to his work upon the movement of sap in plants, and chemists will always recall that several of their common pieces of apparatus owe their development to him. No one previous to HALES had conducted so large a number of experiments upon the growth of various crops and his investigations in this field have for two centuries been a source of inspiration to agricultural chemists in all parts of the world.

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- RAMSAY, WILLIAM (1896): The gases of the atmosphere. London, p. 33.

Jethro Tull (1674-1740):—As the chemist reviews the various theories of plant nutrition which had been proposed up to the time of the publication of HALES' "Vegetable Staticks" he will note that different investigators emphasized some one particular element or factor as of dominant importance. VAN HELMONT, BACON, BOYLE and others selected water as the chief element from which crops derived their nourishment; MAYOW, HALES and their followers focussed attention upon air; STAHL and his school emphasized the importance of the fire-element or phlogiston; GLAUBER and many others of his persuasion attributed everything to nitre; another smaller group, of which WOODWARD was the precursor, called attention to the needs of earth. The leading advocate of the doctrine that earth was the chief factor in nutrition of crops was the celebrated English agricultural writer and farmer, JETHRO TULL.

TULL, who was a close contemporary of HALES, was born at Basildon in Berkshire, England. He studied at Oxford and then prepared for a legal career. He renounced this profession, however, immediately after being called to the bar, and began the practice of agriculture upon his father's farm at Howberry, near Wallingford. In 1701 he invented a machine drill for sowing grain in rows and began his epoch-making experiments upon fine tillage. From 1711 to 1714 he made an agricultural tour in France and Italy where he became strengthened in his belief of the importance of finely pulverizing the soil. Upon the basis of his long experience and extensive observation both at home and abroad he published in 1731 his "Horse-Hoing Husbandry" which was followed by his more complete treatise, "Horse-Hoing Husbandry: or an Essay On the Principles of Tillage and Vegetation Wherein is shewn A Method of introducing a Sort of Vineyard-Culture into the Corn-Fields, In order to Increase their Product, and diminish the common Expense; By the Use of Instruments described in Cuts. By J. T. Cum Privilegio Regiae Majestatis. London: 1733." This work, through its numerous editions and translations, exerted a wide influence for many decades. It is to the 1733 edition that the following citations refer.

Chapters I and II of TULL's book are devoted to a discussion of the functions of the roots and leaves of plants. TULL adopts the view that the pressure of the soil upon the roots of plants forces fine particles of earth into their pores or openings which he compares with the lacteal vessels of an animal's intestines. The greater degree of fineness, to which the earth particles are reduced by tillage, the greater will be the amount of nutritive matter absorbed by the roots. The leaves of the plant, according to TULL, perform a double purifying and excretory function:—

"Leaves are the Parts, or Bowels of a Plant, which perform the same Office to Sap, as the Lungs of an animal do to Blood; that is, they purify or cleanse it of the Recrements, or fuliginous Steams, received in the Circulation, being the unfit Parts of the Food; and perhaps some decay'd Particles, which fly off the Vessels, thro' which Blood and Sap do pass respectively. Besides which Use, the Nitroaerious Particles may there enter, to keep up the vital Ferment or Flame" (*loc. cit.*, p. 7).

TULL's allusion to the possible respiratory function of the leaves in absorbing "nitro-aerious particles" from the air owes its origin perhaps to the ideas of MAYOW. In a footnote (p. 9) TULL criticizes in racy language the view of HALES that the sap of plants does not circulate. In his Chapter III upon the "Food of Plants" TULL reviews the current theories of crop nutrition.

"The chief Art of a Husbandman is to feed Plants to the best Advantage; but, how shall he do that, unless he knows what is their Food? By Food is meant that Matter, which being added and united to the first Stamina of Plants, or Plantulae, which were made in little at the Creation, and gives them, or rather is their Increase.

"Tis agreed, that all the following Materials contribute, in some manner, to the Increase of Plants, but 'tis disputed which of them is that very Increase or Food. 1. Nitre. 2. Water. 3. Air. 4. Fire. 5. Earth.

"I will not mention, as a Food, that acid Spirit of the Air, so much talk'd of; since by its eating asunder Iron Bars, it appears too much of the nature of Aqua Fortis, to be a welcome Guest alone to the tender Vessels of the Roots of Plants.

"1. Nitre is useful to divide and prepare the Food, and may be said to nourish Vegetables in much the same manner as my Knife nourishes me, by cutting and dividing my Meat: But when Nitre is apply'd to the Root of a Plant, it will kill it as certainly as a Knife misapply'd will kill a Man; which proves, that Nitre is, in respect of Nourishment, just as much the Food of Plants, as white Arsenick is the Food of Rats. And the same may be said of Salts.

"2. Water, from VAN-HELMONT's Experiment, was by some great Philosophers thought to be it. But these were deceived, in not observing that Water has always in its intervals a charge of Earth, from which no Art can free it. This Hypothesis having been fully confuted by Dr. WOODWARD, No-body has, that I know of, maintain'd it since: And to the Doctor's Arguments I shall add more in the Article of Air.

"3. Air, because its Spring, &c. is as necessary to the Life of Vegetables, as the Vehicle of Water is; some modern Virtuosi have affirm'd, from the same and worse Arguments, than those of the Water-Philosophers that Air is the Food of Plants. Mr. BRADLEY, being the chief, if not only Author, who has Publish'd this Phantasie, which at present seems to get ground; 'tis fit he should be answer'd, and this will be easily done, if I can shew, that he has answer'd this his own Opinion, by some or all of his own Argument . . ." (*loc. cit.*, pp. 10-11).

"Mr. BRADLEY and all Authors, I think, are of Opinion, that Plants of different Natures, are fed by a different sort of Nourishment; from whence they aver, that a Crop of Wheat takes up all that is peculiar to that Grain; Then a Crop of Barley all that is proper to it; next a Crop of Pease, and so on, 'till each has drawn off all those Particles which are proper to it; and then no more of these Grains will grow in that Land, 'till by Fallow, Dung, and Influences of the Heavens, the Earth will be again replenish'd with new Nourishment, to supply the same sorts of Corn over again. This if true (as they all affirm it to be) would prove, that the Air is not the Food of Vegetables. For the Air being in itself so Homogeneous as it is, could never afford such different Matter as they imagine, neither is it probable, that the Air should afford the Wheat, Nourishment more one Year, than the ensuing Year. Or that the same Year it should nourish Barley in one Field, Wheat in another, Pease in a Third, but that if Barley were sown in the Third, Wheat in the First, Pease in the Second, all would fail. Therefore this Hypothesis of Air for Food, interferes with, and contradicts this Doctrine of Necessity of changing Sorts.

"I suppose, by Air, they do not mean dry Particles of Earth, and the Effluvia which float in the Air, the Quantity of these is too small to augment Vegetables to that

Bulk they arrive at. By that way of speaking they might more truly affirm this of Water, because it must be like to carry a greater quantity of Earth, than Air doth, in proportion to the difference of their different specifick Weight; Water being about 800 times heavier than Air, is likely to have 800 times more of that Terrestrial Matter in it; and we see this is sufficient to maintain some sorts of Vegetables, as Aquaticks. But the Air, by its charge of Effluvia &c. is never able to maintain or nourish any Plant . . ." (*loc cit.*, p. 12).

"If, as they say, the Earth is of little other use to Plants, but to keep them fix'd and steady, there would be little or no difference in the value of Rich and Poor Land, Dung'd or Undung'd; for one would serve to keep Plants fix'd and steady, very near, if not quite as well as the other.

"If Water or Air was the Food of Plants, I cannot see what necessity there should be of Dung or Tillage.

"4. Fire. No Plant can live without Heat, tho' different degrees of it be necessary to different sorts of Plants. Some are almost able to keep Company with the Salamander, and do live in the hottest exposures of the hot Countries. Others have their abode with Fishes under Water, in cold Climates: for the Sun has his Influence, tho' weaker upon the Earth cover'd with Water, at a considerable Depth, which appears by the Effect the vicissitudes of Winter and Summer have upon Subteraqueous Vegetables . . ." (*loc cit.*, pp. 12-13).

"Fire is a fluid *sui Generis*; but that it pervades all Bodies, and there remains Latent; if excited by Violence is Hot; if at Rest may be Cold, being against the essential property of Fire: That Notion cannot pervade the Skull of a Peasant to make him believe, Fire can ever be cold.

"But if we define Fire to be the action of Burning, not the matter which Burns, then Fire will be as different from the Food of Plants, as Air is . . .".

"5. Earth. That which nourishes and augments a Plant, is the true Food of it. Every Plant is Earth, and the growth and true increase of a Plant is the Addition of more Earth.

"Nitre (or other Salts) prepares the Earth; Water and Air move it, by conveying and fermenting it in the Juices, and this motion is called Heat.

"When this additional Earth is assimilated to the Plant, it becomes an absolute part of it.

"Suppose Water, Air, and Heat, could be taken away, would it not remain to be a Plant, tho' a Dead one?

"But suppose the Earth of it taken away, what would then become of the Plant? Mr. BRADLEY might look long enough after it, before he found it in the Air amongst his specifick or certain Qualities.

"Besides, too much Nitre (or other Salts) corrodes a Plant; too much Water drowns it; too much Air dries the Roots of it; too much Heat (or Fire) burns it; but, too much Earth, a Plant never can have, unless it be therein wholly buried; and in that Case it would be equally misapply'd to the Body, as Air or Nitre would be to the Roots.

"Too much Earth, or too Fine, can never possibly be given to Roots, for they never receive so much of it, as to surfeit the Plant, unless it be depriv'd of Leaves, which, as Lungs, should purify it.

"And Earth is so surely the Food of all Plants, that with the proper share of the other Elements, which each Species of Plants requires, I do not find but that any common Earth will nourish any Plant.

"The only Difference of Soil (except the Richness) seems to be the different Heat and Moisture it has; for if those be rightly adjusted, any Soil will nourish any sort of Plant . . .".

"There is no need to have recourse to Transmutation; for whether Air or Water, or both, are Transform'd into Earth or not; the thing is the same, if it be Earth when the Roots take it; and we are convinced that neither Air nor Water alone, as such, will maintain Plants.

"These kind of Metamorphoses may properly enough be consider'd in Dissertations purely concerning Matter, and to discover what the Component Particles of Earth are; but not all necessary to be known, in relation to the maintaining of Vegetables" (*loc cit.*, pp. 13-14).

TULL devotes Chapter V of his treatise to the subject of Dung. He deprecates upon the whole the use of this product as a fertilizer, holding its effect to be purely mechanical and that it injures the flavor of vegetable foods, encourages destruction of crops by worms and adds little to the nourishment of plants:—

"All sorts of Dung and Compost contain some Matter, which, when mixt with the Soil, ferments therein; and by such Ferment dissolves, crumbles, and divides the Earth very much; This is the chief, and almost only Use of Dung; For as to the pure earthy Part of it, the Quantity is so very small, that, after a perfect Putrefaction, it appears to bear a most inconsiderable Proportion to the Soil it is design'd to Manure; and therefore, in that respect, is next to Nothing.

"Its fermenting Quality is chiefly owing to the Salts wherewith it abounds, but a very little of this Salt applied alone to a few Roots of almost any Plant, will (as, in my Mint Experiments, it is evident common salt does) kill it.

"This proves, that its use is not to nourish, but to dissolve, i.e., Divide the Terrestrial Matter, which affords Nutriment to the Mouths of vegetable Roots" (*loc. cit.*, p. 18).

Chapter VI of TULL's work treats of Tillage which according to its author is the most effective means for increasing the food supply of crops. It accomplishes this result by rendering the soil particles more available as food, by making the soil more porous for the extension of root growth and by destroying weeds which rob crops of their nourishment:—

"Tillage is breaking and dividing the Ground by Spade, Plow, Hoe, or other Instruments, which divide by a sort of Attrition (or Contusion) as Dung does by Fermentation.

"By Dung we are limited to the Quantity of it we can procure, which in most Places is too scanty.

"But by Tillage, we can enlarge our Field of Subterranean Pasture without Limitation, tho' the external Surface of it be confin'd within narrow Bounds" (*loc. cit.*, p. 21).

In order to prove that weeds curtail the growth of crops by robbing them of plant food and not of space in which to grow TULL conducted the following experiment:—

"Let Three Beds of the same Soil; equal, and equally prepared, be sown with the same Sort of Corn. Let the First of these Beds be kept clean from Weeds: In the Second, Let a Quantity of Weeds grow along with the Corn; and in the Third, Stick up a Quantity of dead Sticks, greater in Bulk than the Weeds.

"It will be found, that the Produce of the Corn in the First, will not exceed that of the Third Bed; but in the Second, where the Weeds are, the Corn will be diminish'd in Proportion to the Quantity of Weeds amongst it.

"The Sticks, having done no Injury to the Corn, shew there was Room enough in the Bed for Company to Lodge, would they forbear to Eat; or else (like Travellers in Spain) bring their Provision with them to their Inn, or (which would be the same thing) if Weeds could find there, some Dish so disagreeable to the Palate of the Corn, and agreeable to their own, that they might Feed on it without Robbing, and then they would be as Innocent as the Sticks, which take up the same Room with the Weeds" (*loc. cit.*, p. 38).

Expositions of passages in the old Roman agricultural works, notes upon the cultivation of special crops, economic advantages of the new husbandry, and detailed descriptions of plows, drills and other implements with many fine plates of illustrations are among the other topics discussed by TULL in his treatise. Although his views are often erroneous, the

originality of his opinions, the fullness of his observations and the caustic humor of his style make his "Essay on the Principles of Tillage and Vegetation" one of the great agricultural classics.

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Chapter IV

AGRICULTURAL CHEMISTRY IN THE EARLY PHLOGISTON PERIOD

Johann Joachim Becher (1635–82):—At the time when BOYLE and his colleagues of the recently formed Royal Society were striking out into new fields of discovery, there was being initiated in Germany another movement that was destined to play a dominant part in the history of chemistry during the next century. This was the concept of phlogiston which owed its origin to the work of BECHER, an energetic, restless spirit of irritable disposition who, though holding numerous positions of importance, raised up enemies wherever he went. He finally left Germany and sought refuge successively in Austria, Holland, and England. He died at the early age of 47, yet in this short period wrote 16 treatises that remain as evidences of his prodigious industry. Like PARACELSUS and GLAUBER, whom he resembled in so many ways, BECHER was a self-made man and like these predecessors had a supreme contempt for the innumerable speculations (“tausenderley Speculationes”) of the higher schools of learning.

“The most subtle philosopher,” he remarked, “however minutely he may inquire into agriculture and vineyarding, will never bring anything to pass, while the unlettered vinedresser or peasant, who simply obeys nature, cultivates his field and reaps a harvest” (BECHER 1755, p. 31).

BECHER accepted in general the doctrines of four elements and three principles, which he modified, however, in several details. He supposed water and earth to be the primary sources of terrestrial bodies. Like VAN HELMONT he believed plants to be produced entirely from water.

“Rain water,” he declared, “is the generative connatural humor of all plants. It is transmuted not only into their substance but even into their seeds. Plants are nothing else but coagulated rainwater” (*loc. cit.*, p. 77).

In the formation of metals, etc., from the first primeval matter BECHER imagined a progressive evolution to occur. He supposed the *materia prima*, which corresponds to the Yliaster of PARACELSUS, to be divided first into the *materia remota* to which the so-called four elements belonged. The *materia remota* passed next into the *materia media* and the latter in turn into the *materia proxima* to which belonged the actual formative principles of all material objects. In accordance with this view metals, minerals, etc., were being constantly generated within the earth.

In place of the three formative principles — sulfur, mercury and salt — of the iatro-chemists, BECHER substituted the respective terms *terra pinguis* (fatty earth), *terra mercurialis* (mercurial earth) and *terra lapidea* (stony earth). The combustibility of bodies he attributed to the fatty earth, which was expelled by fire. The fusibility of metals he attributed to the presence of the mercurial earth. The stony earth was the residue or calx which was left after the expulsion of the fatty earth of metals and other substances by ignition. These substitutions, although only a change in name, were nevertheless an advance, as the trouble from confusing potential qualities for actual substances (as sulfureous meaning combustible for ordinary

sulfur) was avoided. BECHER held that the immense number of material substances were of a compound nature (*Corpora mixta*). Living things were also *corpora mixta* but because of their higher faculties and more complex nature should be considered in a separate class from the inanimate.

"Other bodies, however, as vegetables, brute animals and men are also indeed *corpora mixta* but in so far as they have something better and higher, independent of and exceeding the mixture, cannot to this extent be strictly called mixed, but each has its name and peculiar form according to its own faculties" (*loc. cit.*, p. 5).

BECHER wrote many of his works in a mixed jumble of archaic German and Latin—a style which some critics attribute to the pedantry of the age but which is probably more the result of an effort to conform to a model of chemical writing that had been set by PARACELUSUS. The following sentence, the original of the passage just translated, is a good illustration of his style:—

"Andere *Corpora* aber, als die *Vegetabilia*, *Animalia bruta et Homines*, seynd auch wohl *Corpora mixta*, aber diewell sie ohne, und über die *mixtion* etwas bessers und herrlichers haben, so werden, noch können sie eigentlich nicht *mixta* genannt werden, sondern haben ihren Nahmen und *formam propriam* aus derselben *facultatibus*."

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Georg Ernst Stahl (1660-1734):—The phlogiston doctrine owes its development not to BECHER but to his pupil G. E. STAHL who accepted his master's teaching that all substances which are changed by ignition contain a common combustible matter or *terra pinguis*. It was to this fatty earth of BECHER that STAHL gave the name phlogiston (from the Greek *φλογιστόν* meaning combustible) which, attached to the school that he founded, became the rallying point of nearly all the great chemists of the eighteenth century.

Like VAN HELMONT, BECHER and many other early chemists, STAHL was a physician. He graduated in 1683 from the University of Jena where he lectured until 1694 when he accepted an appointment at the newly established University of Halle where he taught medicine and chemistry with remarkable success for the next twenty-two years. Many future chemists were inspired by his teaching. In 1716 STAHL was called to Berlin as Royal Court Physician and continued at this post until his death but without relinquishing his interest in chemistry.

STAHL deserves to rank as one of the greatest chemists of history, for it was he who first attempted to construct a rational system of chemistry upon the basis of the experimental observations of his predecessors. Although his system in the end was proved to be wrong, it served nevertheless a most useful purpose in promoting the new discoveries that led eventually to the great reconstruction of chemistry by LAVOISIER. STAHL wrote seven principal treatises upon chemistry of which his "*Fundamenta Chymiae*"

Steph. D. G. Delabrosse.

GEORG. ERNEST. STAHLII,
Confiliar. Aulic. & Archiatri Regii,

FUNDAMENTA
CHYMIAE

Dogmaticae & experimentalis,
& quidem

tum communioris physicae mechanicae
pharmaceuticae ac medicae

tum sublimioris sic dictae hermeticae atque alchymicae.

Olim

in privatos Auditorum usus posita,

jam vero

Indultu Autoris publicae luci exposita.

Annexus est ad Coronidis confirmationem
Tractatus Isaaci Hollandi de Salibus & Oleis
Metallorum.

N O R I M B E R G Æ,

Sumptibus WOLFGANGI MAURITII
ENDTERI HÆRED.

Typis JOHANNIS ERNESTI ADELBULNERI.

An. MDCCXXIII

FIG. 18. — Title page of STAHL'S "Fundamenta Chymiae", Nuremberg, 1723.

(Nuremberg, 1723) is the best known. This work, which exerted a great influence upon the future of chemistry, begins with STAHL's famous definition of chemistry:—

"Chymia, alias Alchymia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi" (STAHL 1723, p. 1).

"Chemistry, also called Alchemy and Spagiric Science, is the art of resolving mixed or compound or aggregate bodies into their principles and of composing such bodies from those principles."

This definition recognizes two main branches of chemistry—analysis and synthesis. It also divides matter according to its chemical composition into four classes, first the fundamental principles or simple elements, beyond which material substances can be no further resolved. In want of a better system STAHL accepted provisionally the old divisions of four elements and three principles, although recognizing that these classifications were unsound. The union of original principles into simple combinations form the class designated by STAHL as "mixts" (*mixta*). Assuming with BECHER that water and earth were the original elements of which terrestrial objects were composed, STAHL called the first simple combinations of these "mixts", of which only a limited number were supposed to exist. Unions of the primary mixts formed the class of substances designated as "compounds" (*composita*) and the miscellaneous masses of compounds, mixts and first principles, that constitute the material world, formed the final class of "aggregates" (*aggregata*) of which there were an almost unlimited number. STAHL's classification is an elaboration of the scheme proposed by BECHER.

The combination of particles of elementary fire, which STAHL termed phlogiston, with those of earth and water give rise to the large class of combustible substances of plant and animal origin. The expulsion of this elementary phlogiston from its many combinations gave rise according to STAHL to the phenomena of actual fire or combustion. His conception was a return under a different guise to the old idea of HERACLITUS that the element fire was the governing principle of nature. It was a survival of the ancient doctrine, continually reannounced by later writers even into the eighteenth century, that combustion was due to the escape of a concealed elementary fire. His doctrine was the direct antithesis of the one proclaimed by MAYOW who held that fire was the result of a striking out of igneo-aërial particles from their atmospheric combination.

In STAHL's opinion metals were compounds of phlogiston with their calces (*i.e.*, oxides) and when the phlogiston of a metal was expelled by ignition the uncombustible calx was left behind as a residue. If the latter was reheated with a substance supposed to be rich in phlogiston, such as charcoal, the phlogiston passed from the carbon to the calx and the original metal was restored. The fundamental error of the conception, like that of the older doctrine of a combustible sulfur in all inflammable bodies, was due to the confusion of a property with a concrete thing. But unlike the older idea of many different sulfurs, STAHL's phlogiston was a definite substance—the same in all its numerous combinations. Many phlogistonists were aware of the fact that metals gained in weight during calcination but this did not disturb their method of reasoning, since phlogiston could

be detected only in combination and nothing was known about its own intrinsic properties. It was simply assumed that the escape of phlogiston from a substance involved an increase in weight. STAHL recognized that the presence of air was necessary for the escape of phlogiston, air being the ambient repository to which it was naturally drawn, but expressly stated that air did not seem to be otherwise involved in the act of combustion.

STAHL's views upon the nutritional relationships of plants and animals are clearly stated in his *Opusculum Chymico-Physico-Medicum* (Halle, 1715).

"It is evident from the history of nutrition that vegetables derive the greatest part of the matter, of which their structure is made up, from earth and water. The bulk of the animal body on the other hand is constructed of corpuscles that were derived from digested vegetables and water,—either directly in case of herbivorous and granivorous animals or indirectly in case of carnivorous animals who feed upon animals that were nourished by grasses and seeds.

"A little reflection upon these facts will make it very evident that the matter peculiar to animals is the same substance of which vegetables consist and that the matter of which vegetables are composed is that mixture (*mixta*) which is most abundant in earth with water" (STAHL 1715, p. 336).

After discussing the corpuscular nature of water and earth STAHL continues:—

"But that species of primordial corpuscles, which in their mixture with earths produce colors and in their mixture with earths and water form oils and fatness (*pinguedinem*), is the species which I call phlogiston, whose appropriate and native seat in my opinion is most largely in the air itself" (STAHL 1715, p. 337).

In other words it is to the union of phlogiston with different earthy calces that the varied colors of the different metals are due and to the union of phlogiston with different earths and water that oils and other inflammable substances owe their combustible nature.

In his discussion of friable earths in which he placed loams, clays, marls, etc., STAHL makes a classification of soils upon the basis of cohesiveness.

"It wou'd be very tedious, and of no great significancy in Chemistry, to enumerate all the particular differences of these Earths: It may be sufficient to observe the distinctions that more immediately regard us, as arising from a different tenuity, and consequently a different degree of mobility, in the Aggregate; whence some Earths are hungry, others fat, some opaque, others transparent, some shining, and others dull.

"The Bolar Earths in particular are either hungry or fat; but seldom found pure and simple, or without the admixture of Salts. All the Earths however of this denomination, differ only as the tenuity of their small separate particles renders them more or less aggregative. An Example whereof we have in common Loam, which by the Potters is called a short Earth, because in the Aggregate it does not cohere tenaciously, so as, upon bare wetting, to concreate into viscous glebes; yet the glebes form'd of it by the admixture of Water, come in some measure into a mass; but so, that if the Water be now separated from it again, it easily crumbles and falls back into its single constituent parts.

"To this Class belong all the hungry Garden Earths, all the sandy Field Earths, and such as are composed of a mixture of both.

"The reason why any Aggregate hereof so easily falls asunder, as we just now hinted, arises from the different aggregative magnitude of all the small parts, and the consequent inequability of their accidental and fortuitous figure; upon which account such particles cannot come into close contact, with broad and flat surfaces and angles, that mutually meet each other.

"Of this we have an experimental demonstration in all these kinds of Earths; for if any of them be reduced to a great degree of fineness by trituration, and then work'd up into a mass by the means of Water, they will now cohere in a much greater degree of compactness, than when the Earth was coarser in its small parts.

"Upon the same Experiment likewise depends what we just now observed of the considerable cohesion, whereby such simple masses of Earth are made pretty strongly to hold together by the bare interposition of Water; tho' in reality this may commonly be owing to the admixture of a saline Substance. Thus, to instance in *Terra sigillata*, which is of the class of Boles or Loams above-mention'd, the cohesion is pretty strong; but if that Earth be committed to distillation in a vessel that is long kept red-hot by the Fire, there at last comes over a small quantity of a humid Acid, in the form of Spirit of Vitriol or Sulphur; upon which the Earth is taken out exceedingly friable; and what is very remarkable, ever after found deprived of that astringency, whereby when lightly moisten'd, it adhered to the tongue; unless this be some way restored to it by the addition of a like new acid.

"Marl or Clay is distinguish'd by its fatness and viscosity from Loam, which we have noted for a hungry Bolar Earth. And indeed all the marly or clay Earths have a certain mucous tenacity, which makes them differ but little from a real Mucilage, especially in some one part.

"For such Earths are all of them heterogeneous; having for their simple matter some very fine earthy particles, scarce perceivable to the touch; whence they are denominated greasy Earths; but for their more formal or specifical part, a certain acid, saline matter, upon which their effect in separating saline Spirits, and setting them free from their alkaline, or calcarious earthy parts, which bind them up into a dry solid form, principally depends" (STAHL 1730, pp. 229-31).

In the class of attenuated earths STAHL placed various gelatinous substances of plant and animal origin:—

"Among the most attenuated kind of Earths may be reckon'd Gums and Mucilages, consisting of Concretes, with a large proportion of a subtile Earth, a saline and a fat substance.

"These are of two kinds; viz. Vegetable and Animal.

"The Vegetable Gums which flow from several Trees upon the bursting of their bark, as the Cherry-tree, the Plumb-tree, the Peach-tree, &c. are nothing else but the Lympha of these Trees; that is, a Water and very subtile Earth mix'd up with a small quantity of a saline oily Substance; and design'd for the nourishment of the woody parts of the Vegetable.

"This Earth nearly approaches the tenuity of a Salt; whence, being mix'd with a small porportion of Water, which it always retains, it has the transparency of a saline crystalline Substance, and when dissolv'd in a large quantity of Water, thus floats about as a Salt.

"There is a less degree of cohesion and tenacity of both these Substances, viz. the aqueous and the earthy, in the Mucilages of Vegetables; such for instance as are plentifully afforded by Linseed, Quince-seed, Semen Psyllii, &c. which are intermix'd with a pretty large proportion of Oil.

"Two Substances of the like kind are also found in Animals; viz. one that is mucous, and another that is glutinous or gelatinous.

"We have an Instance of the former in the Salival Lymphe, condensed either by too large an evaporation of its aqueous particles, whence the glutinosity of the Saliva observed in ardent and slow Fevers; or else by the admixture of other fine solid particles. Thus upon gently chewing and swallowing Grapes, fresh tart Cherries, or slowly sipping fermenting Must, or hot Wine that is austere and styptic, the Salival Lymphe is condens'd into a mucous tenacity, by the interspersion of the saline, earthy, astringent particles of these Concretes.

"Jellies or Glews are the same kind of Lymphe highly condens'd, that is, greatly depriv'd of its aqueous particles; so that but few of them now remain mix'd with the earthy; whence they turn into a slimy matter, or thin mucilage again, by the addition of such Water.

"'Tis farther to be observ'd, that these gummy or gelatinous animal Substances are mix'd with a larger quantity of alkaline oily Salt, and thence obtain a saponaceous nature.

"The manner wherein both of them are separated and prepared, deserves also to be consider'd.

"We lately observ'd, that the vegetable Gums spontaneously distill'd from Trees, when any external violence has broke their veins or canals: but the animal Gums are fetch'd out of the glutinous parts of Animals, by boiling them in fair Water.

"These mucilaginous parts are principally the Flesh of Animals; a parcel whereof being, along with a little Water, put into a pewter body, furnish'd with its screw-head, and the body thus well closed, set into a Copper of boiling Water, and continued there for some hours; if after this it be taken out, and the matter strain'd hot, and exposed to the open Air, it there becomes a solid Substance; the remainder from whence the thinner part was thus express'd, now appearing reduc'd almost to the form of a powder.

"Tho' this Experiment may seem derived from the kitchen, 'twas nevertheless the Foundation of that Machine called PAPIN's Digestor, so much admired at present for softening the Bones of Animals; the operation and instruments being the same in both cases; only perform'd by the Digestor with much greater advantage and convenience.

"Thus the Bones, the Horns, and all the hard or solid earthy parts of animal bodies, are by this Glew, as 'tis more or less dried, compacted into a tenacity or compleat degree of hardness. For if any bony substance, as harts-horn for instance, be strongly boiled with nothing but Water for two or three days in a close vessel; the liquor being poured off at times, especially the first day, and fresh Water put on; the horn will at length fall into a white powder; and if the liquors poured off be exhaled till their superfluous Water is wasted, they leave the Glew behind, which before compacted this white powder into so great a degree of firmness; tho' now very much alter'd in its tenacity by the long boiling" (STAHL 1730, pp. 241-4).

Of the crystalline organic substances obtained from plant juices STAHL describes cane sugar, the process of its manufacture from sugar cane and the method of its raffination. (*loc. cit.*, pp. 111-4.) Following the custom of the times he terms sugar a salt. STAHL also describes the preparation and purification of tartar (*loc. cit.*, pp. 117-21), the deposit from fermented grape juice known to the Greeks and Romans, and to which PARACELUS first gave the name "tartarum". In his description of these technical processes STAHL refers to the "Saccharologia" of ANGELO SALA. The fixed and essential oils, rosin and other plant substances are also described by STAHL.

The subject of fermentation long engaged the attention of STAHL, his "Fundamental Zymotechny or General Theory of Fermentation" (STAHL 1697) being among his earliest published books. His definition of fermentation, at the beginning of Chapter II of this work, continued to be accepted for over a hundred years: —

"Fermentation is a motion of an exceedingly large number of molecules of salt, oil and earth (somewhat closely united although not inseparably so) through an aqueous fluid in a state of collision and friction by which the bonds of their principles are gradually loosened and then as a result of that action, worn and parted by frequent attrition. By the intermingling movements of the particles some of them are joined together anew and when this occurs they are in part projected outside, and in part left behind within the fluid, although they can be removed or drawn off from the same. Or more broadly. Fermentation is an internal motion within a suitable fluid by which concrete particles or different kinds of matter in a loose state of combination are, through violent agitation together, subjected to friction and collision, as a result of which the bonds of the existing combination are torn apart and the separated corpuscles, after having been worn by attrition, are united together in a new firmer combination" (STAHL 1715, pp. 73-4).

In the development of his subject STAHL assumes that in a fermenting aqueous liquid there are particles of fire, air, and oil which are more movable and particles of salt and earth which are less motile than the corpuscles of water. The more movable particles impart a greater agitation to the molecules of water which in turn cause a stronger loosening of the less motile salt and earthy corpuscles. The bonds of connection being stronger in "mixts" than in "compounds" the latter are the first to be resolved by the friction of the moving particles. Since the movements of the more motile corpuscles are slackened by contact with the more sluggish ones, it is necessary, when an excess of the latter is present, to hasten the agitation of the particles by conducting the fermentation in a warm place. On the other hand if the more motile so-called "oily" particles are in excess the agitation may be too strong in which case the fermentation should be retarded by conducting it in a cool cellar. According to STAHL the phlogiston of the fermenting liquid became localized in the inflammable spirit which could be separated by distillation.

STAHL's treatment of inorganic chemistry is upon the whole mechanistic. He held that chemistry should be studied not according to imaginary geometrical relations but with reference to the physical states of matter and for this point of view was the first to coin the expression "physical chemistry". Like most chemists of his time STAHL was a believer in transmutation and wrote a treatise upon "The Philosopher's Stone". He remarked, however, that

"As for the thing itself, or the bare manner of preparing Philosophical Gold, we physically esteem it much less considerable than the sowing of Corn, or the making of Bread" (STAHL 1730, p. 424).

In his treatment of the chemistry of living bodies STAHL followed to a certain extent the mystical philosophy of VAN HELMONT. He believed that the chemical processes of digestion, assimilation, etc., were directly regulated by the "sensitive soul" (*anima sensitiva*) which pervaded all parts of the body. This conception was especially developed in his treatise "On the real difference between a mixed substance and a living body" (*De mixti et vivi corporis vera diversitate*). VAN HELMONT also held the idea of a controlling soul which acted through the agency of archaei and the latter in turn through ferments. STAHL rejected the archaei of PARACELUS and VAN HELMONT entirely and, although recognizing the existence of ferments, emphasized the distinction between ordinary fermentation and the process of digestion:—

"The fermentation which takes place in the alimentary canal is not an ordinary fermentation such as occurs in a merely compound non-living body, but a most special character is impressed on the change, impressed by the energy of the soul."

STAHL's conception of a sensitive soul that controlled the chemical processes of living matter gave birth to that special branch of the vitalistic philosophy known as "animism", survivals of which under various forms have come down to the present day.

It is somewhat remarkable that STAHL made little effort toward applying his chemical knowledge to explaining the phenomenon of respiration. The heat of the blood he attributed to the friction of its circulation and not

to any chemical action. He seemed to think that air might contribute some material substance to the body during respiration but he then adds:—

"Meanwhile it is wholly clear, from every point of view, that that something is neither great in quantity nor dense in quality, nor indeed anything different from the true nature of atmospheric air, which it must necessarily be if breathing supplied any kind of spirit to the blood. If it be anything it must be something much more simple, namely a certain principle called phlogiston. Nevertheless in respect even to this, doubts against it of no less weight than arguments in favour of it present themselves. For this principle does not abound in the air in sufficient quantity to be able at each breath to supply and add to the blood an amount of itself of any moment. This is *a posteriori* clear from the fact that only a very little of this matter of phlogiston can be received into even a large quantity of air, even in a place where it is sufficiently collected in it, as when inflammable things are burnt. However, these things may be, these considerations, interesting perhaps to the curious, add absolutely nothing to medical practice; and it is not meet to waste any more time upon them" (FOSTER 1901, pp. 226-7).

"Thus," as Sir MICHAEL FOSTER remarks, "the great exponent of the chemistry of his time, and especially of the chemistry of combustion, touched lightly the key to one of the most important of the chemical problems of the living body and having touched it, deliberately drew his hand away."

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- (1723): *Fundamenta Chymiae dogmaticae et experimentalis, et quidem tum communioris physicae mechanicae pharmaceuticae ac medicae tum sublimioris sic dictae hermeticae atque alchymicae*. Olim in privatos Auditorum usus posita, jam vero indultu Autoris publicae luci exposita. Norimbergae.
- (1730): *Philosophical Principles of Universal Chemistry, or The foundation of a scientific manner of inquiring into and preparing the natural and artificial bodies for the uses of life; both in the smaller way of experiment and the larger way of business*. Design'd as a general introduction to the knowledge and practice of artificial philosophy or genuine chemistry in all its branches. Drawn from the Collegium Jenense of Dr. GEORGE ERNEST STAHL by PETER SHAW. London, John Osborn and Thomas Longman.

Herman Boerhaave (1668-1738):—One of the greatest figures in the transition period of chemistry, when old theories were being tested in the light of new knowledge, was HERMAN BOERHAAVE of the University of Leyden. Although distinguished chiefly as a physician, he was, like many of his famous contemporaries, broadly trained and won eminence not only in medicine but in chemistry, botany and other sciences. He was especially skilled in chemistry and, although he made no new discoveries in the science, his "*Elementa Chemiae*" owing to its clarity and fulness of treatment, soon became the leading text-book upon the subject. It was translated into many languages and its numerous editions exercised a wide influence for over half a century. Owing to its copious references to the

composition and analysis of plant and animal products BOERHAAVE's book appealed especially to those who were interested in the applications of chemistry to agriculture.

The first edition of BOERHAAVE's lectures upon chemistry was published in an unauthorized Latin edition at Paris in 1724 (English translation by SHAW and CHAMBERS in 1727). BOERHAAVE repudiated the authenticity of this work and in 1732 brought out his own "Elementa Chemiae" which was translated by SHAW under the title, "A New Method of Chemistry" (editions of 1744 and 1753). It is from the two quarto volumes of the 1753 edition that the following extracts are taken.

Part I of BOERHAAVE's "Elementa" contains a history of chemistry (64 pages) which is one of the best accounts of the early development of the science that has ever been written. Part II of the book (529 pages) is devoted to the theory of chemistry as related to metals, salts, minerals, vegetables, and animals and to the operations and instruments of chemistry. Part III, upon the Practice of Chemistry, describes 88 laboratory Processes for examining vegetable products (expressed and essential oils, waxes, balsams, gums, resins, camphor, honey, tartar, fermented and distilled liquors, vinegar, plant ash, etc.), 39 laboratory Processes for examining animal products (milk, urine, albumen, blood, etc.) and 100 laboratory Processes for examining mineral products (salts, sulfur, metals, etc.). Following the detailed description of each Process is an account of its use and application.

BOERHAAVE's theory of plant nutrition is expressed as follows:—

"The root is intended for fastening the plant to the ground, or for imbibing nutriment therefrom. . . . The root is furnished with absorbent vessels, whose mouths are ranged close to each other thro' its whole surface, by which the nutritious moisture is imbibed, protruded into the canals, and by these conveyed thro' the whole substance of the plant. These vessels may properly be compared to the mesenteric lacteals, and other absorbent veins of animals. The juice thus derived from the alimentary body is not yet of the proper nature of vegetables, but being crude, retains the disposition of the mother from whence it was drawn; yet this, which is usually earth, or water, receives back, sooner or later, whatever it had imparted; in as much as bodies generated from the earth and water, when at last they decay and die, return again into air, water and earth. . . . Water, spirits, oils, salts, and all other bodies are hid in the earth, where being agitated and mixed, especially with water; by subterraneous, artificial and solar fire they are brought to the roots of plants spread in the ground. . . . The same juice being afterwards agitated by the structure of the plant, the fire, both subterraneous and solar, the oscillations of the air, the vicissitudes of moist, dry, cold and hot weather, and the changes of day, night, and seasons of the year, is protruded thro' the several vessels of the plant; and thus gradually changed and further elaborated so as to form a new and peculiarly vegetable juice proper to each part of the plant. The leaves, by the structure, number, and fineness of their vessels, expose their finest juices almost naked to the air, in a surface much enlarged; which is liable to be actuated from divers causes. By such means these juices are extremely altered and by further coction reduced to a peculiar vegetable nature; in fine, they do the office of lungs" (*loc. cit.*, Vol. I, pp. 135-40).

In the first unauthorized edition of BOERHAAVE's chemistry is an additional statement regarding the movement of plant juices:—

"The juice having thus gone its stage from the root to the remote branches and even the flower; and having, in every part of its progress, deposited something, both for aliment and defence; what is redundant, passes out into the bark, the vessels whereof are inosculated with those wherein the sap mounted; and thro' these it redescends to

A
NEW METHOD
OF
CHEMISTRY;
Will. INCLUDING THE *Lipsip. 1755*
History, Theory, and Practice
of the ART:

Translated from the ORIGINAL LATIN of
Dr. B O E R H A A V E's
ELEMENTA CHEMIÆ,
As PUBLISHED BY HIMSELF.

To which are added,
NOTES; and an APPENDIX,
SHEWING
The NECESSITY and UTILITY of
Enlarging the Bounds of CHEMISTRY.
WITH SCULPTURES.

By PETER SHAW, M. D. F.R.S.

THE THIRD EDITION Corrected.

L O N D O N:

Printed for T. and T. LONGMAN, in *Paternoster-Row*,
MDCCLIII.

FIG. 19. — Title page of BOERHAAVE's "New Method of Chemistry", 3rd English Edition by PETER SHAW, London, 1753.

the root, and thence to the earth again. And thus a circulation is effected" (1727 Ed., p. 145).

The suggestion that the redundant part of the plant nutrients "redescends to the root and thence to the earth again" is one of the earliest references to the possible excretory function of roots—a theory, which elaborated a century later by DE CANDOLLE, SPRENGEL, LIEBIG and others, was destined to play a significant rôle in agricultural chemistry.

Although a man of progressive outlook BOERHAAVE was still influenced by many of the old traditions. He cast loose from the teachings of the iatro-chemists, yet was a believer in the transmutation of metals and in the ancient quaternary of elements. He drew, however, a careful distinction between elementary fire, earth, etc., and the common things so designated. Adopting the revived atomic theory of DEMOCRITUS he believed atoms or corpuscles of elementary fire to be contained in all things and that by friction of wood, metal, stones, etc., these elementary particles were made to coalesce as shown by the manifestation of heat. If the friction of wood was long continued the union of a sufficient number of the elementary fire particles caused the production of flame. In this way BOERHAAVE explained the spontaneous heating and combustion of hay and other plant materials (a phenomenon which is still the subject of investigation by agricultural chemists), the coalescence of the fire particles being produced, as he thought, by the internal friction of the fermenting material. BOERHAAVE'S chemical investigation of this phenomenon is quoted as an example of his methods of experimentation, analysis, and discussion: —

"PROCESS LXXXVIII

The Putrefaction of vegetables

"If the soft, fresh, and juicy parts of vegetables, be in the summer-time thrown into an open cask, and pressed down therein, that the vessel may be almost full, and then left thus in the open air, they will soon of their own accord, begin to grow warm, and continue to do so more and more every day, especially in the middle. This heat, at length, increases above that of boiling water, and proves so much the more violent, the more the matter was compressed, and the less aqueous the plants, provided they were not dry. After this heat is arrived to its height, it again decreases by degrees, and returns to the temperature of the atmosphere: and by this means, the whole mass of vegetables is reduced almost to an uniform, pappy mass. This heat begins in the middle of the heap, where it is greatest, and thence spreads itself every way, till at length it possesses the whole. It makes no difference what plants are employed for this purpose, whether the most alkaline, as scurvy-grass; the most acid, as sorrel; or the most insipid, as grass. These plants first breathe their own odour, if they were fragrant, so long as the heat continues small, or not above eighty degrees; and so long their particular taste remains; but as the heat becomes gradually greater, the natural odour is changed into that observed in hay that grows hot, upon being stacked too wet; and lastly, the heat coming to its height, all the peculiar smell, taste, and even the colour of the plant is lost; a putrid, fetid, stercoraceous smell, and a cadaverous, putrefied taste, resembling putrefied urine, are produced, the presiding spirit is lost; and the smell and taste are the same, tho' the plants were ever so different. If the plant be fresh cut, half dried, or still otherwise retains its natural juices, and be thrown into large heaps, a sharp and very diffusive odour will first arise; which shews that the fiery motion is beginning in the inward part of the heap, where the compression is the greatest, whilst no heat is yet perceived on the outside. If now the whole heap be thrown abroad, and the plant cooled, the putrefaction is presently stopped; but if left to itself in the heap, the heat increases, so as to rot all the inside, boil in the middle, and at length break out into open flame; and the larger the heap, and the greater the weight,

the sooner this putrefaction and fire is produced. If the matter thus takes flame, it is changed, as it would be, by burning under a chimney; but if it be strongly heated, tho' not so far as to fire, it then perfectly putrefies into a pap, as in the case we have described; and hay is too frequent an example hereof. This action comes on the slower in vegetables, the more dry they are of themselves, or the more they have been dried; but if moistened with an additional quantity of water, so as to grow thoroughly wet, the putrefaction will renew in them again. It also proceeds the slower, the lighter the matter lyes upon itself, so as to leave spaces that admit the free air; but it proceeds the more strongly, the softer the subject, and the more violently compressed. Whence the drier plants, such as rosemary, being put up into a cask, will scarce putrefy in the manner above described, unless strongly pressed down by weight, or unless the heap were large. On the other hand, if too aqueous, a certain corruption, but not this heating action, is usually produced. If this pappy mass, so prepared, be immediately put into a large glass body, and distilled, with the junctures well closed, almost to dryness; a limpid, fetid liquor will come over, that should be kept separate. Put the remainder, now almost dry, into a glass retort, and distil with degrees of fire, to the highest that can be given in sand; and thus it affords white fumes, a large quantity of liquor, a white salt, and a black thick oil; all to be kept apart. There remains behind a very small quantity of black faeces, which being taken out, and burnt in the open fire, leave a mere earth, without any fixed salt behind; tho' this salt might be obtained, in plenty and perfection, from the same plants before putrefaction.

"If, when the oil is separated, the last liquor be, with a gentle fire, distilled, in a tall vessel, to an half, it affords a sharp, alkaline, saline, volatile spirit; which again being distilled to an half, becomes much stronger. And if the operation be repeated in a close vessel, a liquor will at length be obtained, extremely like rectified spirit of hartshorn; and afterwards by a gentle fire, a true volatile salt, in greater plenty than the plant would have afforded, of fixed salt by burning, before putrefaction. The like spirit and salt may be also obtained in the same manner, from the former liquors; and when thoroughly purified, they perfectly resemble the volatile salt, and spirit of animals, without the least chemical difference; and this happens, even tho' the plant were of the most acid kind. The oil, forced over by the last extremity of the fire, is black, thick, and intolerably and lastingly fetid; in which respects, as also in its pitchy tenacity, it extremely resembles that which, by the utmost violence of fire, is separated from animal subjects.

"The use

"The action above explained is called putrefaction; which, without the assistance of art, spontaneously happens in vegetables, as often as they are thrown on large heaps, or compressed in a moist state. . . . This putrefaction is carefully to be distinguished from fermentation; the rather, because artists every where too much confound them, to the detriment of arts. The differences appear to be these, (1) A greater grossness, compression, and density, seems required in the putrefaction, than in the fermentation of vegetables. (2) Putrefaction acts upon all vegetables whatsoever, provided they be soft and juicy; but fermentation only upon some, and not upon others. (3) The heat required in putrefaction spontaneously rises from the degree of an healthy human body, even to that of a violent flame; but in fermentation, if the degree of heat rises up to that of an healthy body, the fermenting cause is dissipated, and the liquor turned vapid; for the heat, generated by fermentation, is not greater than that of seventy five degrees, except in the fermentation of vinegar; and even there, unless the heat be immediately stopped, no vinegar, but a corrupt vapid liquor will be obtained. (4) Putrefaction renders all the saline matters volatile and alkaline, the oils fetid and volatile, and almost volatilizes the earth itself: but fermentation makes acids volatile, and subtile, and, contrary to alcalies, spirituous, gratefully odorous and inflammable: it generates an acid tartar, that leaves an alkaline matter, as fixed in the fire as the subject would have done before. (5) The salts that by putrefaction are of the same simple, alkaline, fetid, volatile nature, are by fermentation acid, in great measure fixed, and compounded of spirit, oil, and earth. (6) Putrefaction is a means of entirely converting all the saline vegetable matters, into one and the same simple, volatile alcali; but fermentation converts only a certain little part of the saline matter of vegetables, into a liquid, volatile acid, leaving the rest almost unchanged" (1753 Ed., Vol. 2, pp. 180-3).

BOERHAAVE's description of the spontaneous heating and ignition of hay is a good illustration of his accuracy of observation; his distinctions between fermentation and putrefaction are carefully thought out; and his methods of analysis, though crudely qualitative, show a great advancement over previous work of a similar kind. His reference to the loss of the presiding spirit (*Spiritus rector*) shows that BOERHAAVE, with all his repugnance to mysticism, could not wholly escape from these vitalistic conceptions which in different forms have continued to appear in the history of chemistry from the time of PARACELSUS down to the present. The presiding spirit, or *aura*, although imponderable, was yet held by BOERHAAVE to be revealed by means of its chemical effects: —

"By chemistry then, alone, it is we learn, that in every animal, or vegetable, there is a certain *Aura* or spirit, peculiar to that single body; so subtle as only to be perceived by its smell or taste, or other effects not found in any other. This *Aura* exhibits the proper character of that body, whereby it is accurately distinguished from all others; it is too fine and thin to be seen by the eyes, though arm'd with a microscope, or felt by the hands, and withal is extremely volatile; so that when pure and single it flies off, by its greater mobility mixes with the air, and returns into the common chaos of all volatiles; there still retaining its nature, it floats till it falls down with snow, hail, rain, or dew; by which it again enters the bosom of the earth, impregnates it with its prolific virtue, and at length is received with other juices of the earth into the bodies of animals and vegetables. By such revolution it passes into new bodies, whose mass it animates and directs" (1753 Ed., Vol. I, p. 168).

BOERHAAVE's *Spiritus Rector*, or *Aura*, thus corresponds to the Generative Water of PALISSY.

BOERHAAVE's aim, as set forth in the preface of his "Elementa Chemiae", was "to raise chemistry into a rank with the other academical sciences" and this in large measure he accomplished, although the battle for the recognition of chemistry as a science was not finally won until the time of LIEBIG. BOERHAAVE's apology for chemistry, one of the first of many similar defences, is here reproduced for the picture which it gives of the lofty ideals of the first great teacher of chemistry: —

"Of all the sciences chemistry is best adapted for discovering those latent peculiar powers of bodies; whence we may safely conclude, that the chemical art is the best and fittest means of improving natural knowledge. They who are possessed hereof will be able, by a truly active knowledge, to produce physical effects, without resting in subtleties of words, or idle speculation of theory; it being the character of a chemist, that his speculations pass on to effects. Thus, when he explains glass, he will at the same time shew the manner wherein it may certainly be made; and in accounting for fermentation, he will at the same time produce it; his sayings will be effects; and being free from the enquiry of ultimate causes, he will give the present ones. He does not invoke daemons, goblins, or spirits, but applies body to body, and thus works his end. He does not regard the names of substantial forms, but sticks to the consideration of the sensible powers peculiarly found in each body; which he exhibits by effects, and shews how they may be applied to the production of the noblest works. He pays no homage to occult qualities, but discovers by his art the effects ignorantly ascribed thereto; and teaches how, when discovered, they may be brought into action. He readily confesses his ignorance as to the creation of seeds, and the peculiar structure given to each body at its first origin; but carefully attends to the appearances arising therefrom, and after noting them faithfully down, applies them directly to the working changes in things. Such are the noble fruits which chemistry, duly cultivated, holds forth to natural philosophers; and from this will arise such a system of physical knowledge as the great Lord BACON wish'd for, and begun; and which, in persurance

of his design, the immortal Mr. BOYLE considerably promoted" (1753 Ed., Vol. I, pp. 173-4).

BOERHAAVE died in 1738 after having served for 32 years as Professor of Medicine, Chemistry and Botany at the University of Leyden. His knowledge of these sciences and his great fame as a teacher attracted so many students from all parts of Europe that the years of his professorship at Leyden have been called by KOPP (1843) the most splendid period in the history of this university. His great position in chemistry is not due to any strikingly new discoveries but to the spirit of independent leadership which for the first time he gave chemistry in its rank with other sciences. He was not a dogmatist but a man of broad liberal outlook. Although he is generally placed among the phlogistonists, BOERHAAVE was not an assertive member of this school and can be called a follower of STAHL only for the reason that in his lectures and books he expressed no opinion contrary to the basic principles of STAHL's philosophy.

BOERHAAVE's "Elementa" with its predominant stress upon experimental demonstration gave a new impetus to the study of plant and animal chemistry. It offered the most complete critical account of chemical science that had yet appeared and was of such excellence that it continued to be consulted and used as an authoritative laboratory guide for over fifty years after the date of its publication.

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René Antoine Ferchault de Réaumur (1683-1757):—The Baconian movement, which led to the establishment of the Royal Society in England, led also to the founding of the French Académie des Sciences in 1666. This organization after a brief period of indifferent success was reconstituted under more favorable conditions in 1699. One of the leading spirits of the newly reorganized academy was the celebrated scientist RÉAUMUR, who from the time of his election in 1708 until his death in 1757, contributed to its Mémoires a succession of noteworthy papers upon nearly every

branch of pure and applied science. Many of his contributions relate to agriculture and agricultural chemistry. In 1730 he attempted to establish certain indices for diagnosing the fertility of soils. In 1731 he became interested in meteorology and devised the well-known RÉAUMUR thermometer scale in which the freezing point of water is taken as 0° and the boiling point as 80°.

RÉAUMUR employed his thermometer in a long series of investigations upon the spontaneous heating of manure, a material which he utilized for supplying warmth to incubators for hatching eggs. The results of these experiments were presented before the Academy in 1747. An English translation of RÉAUMUR's book upon the subject was published at London in 1750 under the title, "The Art of Hatching and Bringing up Domestick Fowls of all Kinds, at any Time of the Year, either by means of the heat of Hot-beds, or that of Common Fire". This work, which is written in RÉAUMUR's entertaining discursive style, describes not only the construction of incubators and the technique of hatching and rearing chicks, but also discusses the respiration of eggs, the need of adequate ventilation during incubation and other related subjects. The very practical trend of RÉAUMUR's mind is indicated by his study of methods of preserving new-laid eggs. Of the various processes investigated, the following, which is still employed, is the one that he chiefly recommends: —

"Take on the end of your finger the bigness of a pea of either butter or any other fat whatsoever, rub the shell with that fat, and pass and repass your finger over the whole surface of the shell, so as that you may be sure that no part of it was left untouched: when this is done, the egg is perfectly secure against the evaporation, or, which is the same thing, against corruption. Oil is employed for this use with the same facility and parsimony: you dip the end of your finger into oil put in a small saucer or in any other vessel, you rub the shell with the tip of that oily finger, and if the quantity of oil you have taken at first is not sufficient to anoint the shell all over, you dip your finger a second time into the oil, and rub it as before. However, here is a proof that neither the butter, nor the fat, nor the oil need be put over the egg in a quantity sufficient to leave a visible coat of it on the outward surface of the shell; I have many a time wiped with a clean towell eggs after they had been anointed with oil or fat, and they nevertheless remained always fresh" (pp. 413-4).

In addition to his pioneer work upon incubation RÉAUMUR made important studies on the digestion of carnivorous and graminivorous birds. His greatest work is a six-volume magnificently illustrated treatise upon insects (Amsterdam 1734-42) which still impresses the reader with its marvellous attention to accurate, detailed observation.

RÉAUMUR, who was a man of wealth, loved the retirement of his country estates where much of his scientific work was performed. He died on October 17, 1757, as the result of a fall from horseback.

REFERENCE:—

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Henri Louis Duhamel du Monceau (1700-82):— A prominent advocate of TULL's doctrine of fine tillage was the eminent French agricultural writer and scientist, DUHAMEL DU MONCEAU. He was educated at the College of Harcourt, but the courses of instruction at this school did not

suit his scientific aspirations and so, withdrawing from its halls, he lodged near the Jardin des Plantes of Paris where associations with GEOFFROY, LEMERY and other chemists gave the stimulus that prompted his future activities. DUHAMEL's scientific interests covered the range of nearly all the applied sciences. Upon his estate at Denainvilliers he conducted practical studies in agriculture, horticulture, plant-physiology, and meteorology, while as Inspector General of the French Marine he devoted attention to engineering, ship construction, rope-making, wood preservation and many other technological subjects. His governmental position caused him to become deeply interested in the agricultural and industrial resources of France and he became an authority upon national economics.

DUHAMEL for over fifty years was a member of the French Academy of Sciences, in the Memoirs of which for 1737 he published an important article showing the base of common salt to be a true fixed alkali, that occurred in the ash of certain marine plants, as the saltwort (*Salsola kali*), and differed in some respects from the alkali known as potash obtained from land plants. His report of two kinds of fixed alkali was at first disputed but was finally confirmed by MARGGRAF in 1768. In order to ascertain whether this difference in alkali was determined by the nature of the plant or the soil DUHAMEL cultivated saltwort for a number of years upon his inland estate at Denainvilliers where the soil was deficient in salt. It was found after a few years that the alkali in the ash of saltwort in its new habitat consisted almost entirely of vegetable alkali (potash), the mineral alkali (soda) having been largely displaced. This experiment was one of the earliest attempts to prove that plants derived their mineral constituents from the soil and not by the supposed transmuting power of a vital agency.

TULL's principles of tillage were advocated by DUHAMEL in his "Éléments d'Agriculture" (Paris, 1754) from the English translation of which the following passage is quoted:—

"The more the particles of the earth are divided, by so much the more are the internal pores encreased; that the more the surfaces of the particles are enlarged, with so much greater ease do the roots extend; that the better condition the earth is put in to supply plants with food, so much the more fruitful must it of course be rendered.

"It may be added that, by this division, the introduction of the water among the earthy particles is facilitated, over the surfaces of which it would otherwise pass without penetrating them. This division also causes the admission of the air and sunbeams, two agents very necessary to vegetation.

"This division may be two several ways effected: by causing the particles to ferment naturally, which is the effect produced by a mixture of dung with earth; or by mechanically breaking the particles; this is the effect of tillage" (DUHAMEL 1764, pp. 100-1).

DUHAMEL differed from TULL, however, in that he did not overstress tillage but emphasized also the need of crops for dung and other manures—mineral, vegetable, and animal. Among the mineral manures he enumerates earth from ditches, ponds, etc.; air-slacked lime; plaster; and especially marl which he calls an "inexhaustible treasure". Good marl should be friable and acted upon by acids. Because of its supposed warming, cleaning, and sweetening effects DUHAMEL believed marl to be best suited for cold moist soils or such as produce many weeds. The benefits of marl he supposed to last for 30 years. Among vegetable manures DUHAMEL recommended any plants disposed to putrefaction such as buckwheat,

clover, beans, etc., when plowed under. Vegetable residues, such as lye ashes, tan bark, marc of grapes, leaves of trees, linseed cake, and sea weed, are also named. The best results are obtained when vegetable and animal substances are composted together. Among animal manures DUHAMEL mentions slaughter house refuse, bones, horn, old leather, fish scraps, waste of cities, and excreta of all kinds. Dung should be composted with plenty of straw or other litter in pits that are adequately protected from the rain and from losses by seepage.

The very practical trend of DUHAMEL's mind is indicated in all his treatises. He was opposed to quackeries of every kind and particularly to the so-called fructifying liquors, or steepes, for treating seeds before planting. A host of such preparations were advertized in the early eighteenth century. DUHAMEL's opinion of these compounds is given in the following passage: —

"On fructifying Liquors, or Steeps"

"The marvellous is well-relished, particularly when it promises us very useful matters; nothing could be of more advantage than to have good crops without dunging the land, and with very slight tillage this is what the Abbé DE VALLEMONT proposed. By means of his fructifying liquors, the whole attention was to be confined to the preparation of the seed; and when it was once impregnated with a certain liquor which had, as he said, the property of unfolding the buds, a good crop was to be expected. Nothing could be more improbable. It is well known that a seed contains a plant in miniature, in that part called the bud; that the rest is a stock of food to support the young plant, till it has put forth roots enough to draw its nourishment from the earth: no sooner do the roots extend but the seed is exhausted and there remains nothing but the husk, which thenceforward is useless: what effect then can fructifying liquors have? They may, perhaps, make the nutritive substance of the seed more proper for the support of the young plant, which, by that means may, till it has put forth roots, be more vigorous; but when once this young plant has put forth its roots, when once it ceases to be supported by the lobes of the seed, of what use can the fructifying liquors be? Is there the least probability that any of it is to be found at the distance of four or five inches from the plant, in the earth to which the roots are extended, and from which they extract their nourishment? However void of all probability this idea may be, DE VALLEMONT's liquor was esteemed a wonderful discovery; it was looked upon as a magnet capable of attracting from the atmosphere certain principles which probably never existed there; and a number of receipts for making fructifying liquors have been invented. The different books of Agriculture, the *Maison Rustique*, swarm with them: they are there represented as wonders in Nature. The desire the public had to find these virtues real, procured them a good reception; and experiments badly conducted propagated the error still farther.

"They took a certain quantity of seed; they impregnated it with these pretended fructifying liquors; they sowed these seeds, one by one, in a kitchen-garden; they saw a wonderful encrease, and thought it all owing to the liquor. I was myself deceived by such trials; but when I extended them to pieces of three or four acres, this wonderful encrease was no longer visible, and I began to have but little dependence on these boasted liquors. But, having seen a single grain of Barley produce, without any preparation, two hundred and thirty stalks; and being also informed, that another grain of Barley had produced in England one hundred and fifty ears, I thence concluded, that these wonderful encreases, so much boasted of in the *Maisons Rustiques*, and attributed to liquors that unfolded the buds, were to be attributed to the quality of the soil, to good tillage, and to the grains being so distant one from the other, as to be able to extend their roots very far, and collect a great quantity of nourishment. I had then recourse to new experiments, which confirmed me in my opinion.

"I caused some good Wheat to be steeped in the juice of dung, to which I had added lixivial salts, nitre, and sal ammoniac; this grain I sowed in two beds of a kitchen-garden, well dug with the spade; but in one of these beds it was sowed very thick, and in the other very thin. At the same time I sowed two other-like beds with

the same seed unsteeped, after the same manner the steeped Wheat was sowed; one of the beds was sowed very thick, the other very thin.

"At harvest-time the beds that had been sowed with the steeped Wheat, so exactly resembled the others, that it was not possible to distinguish them, without having recourse to the register of my experiments (DUHAMEL 1764, Vol. I, pp. 229-32).

DUHAMEL shows similar good sense and sagacity in discussing the problem of whether different crops abstract in each case a special kind of nutriment from the soil. The doctrine had been advanced that wheat depleted the soil of one kind of nutrient matter, rye of another, barley of another, etc., and that these different crops did not, therefore, compete with each other for their supplies of plant food. DUHAMEL's arguments against this point of view are quoted in part: —

"Whether the several Kinds of Plants require the same Nourishment

"To take this matter in a general sense, it does not seem probable that the same matter can supply such a number of plants with food, which differ one from the other in appearance, in form, smell, taste, and even in their properties: for it is not to be doubted but the internal parts of plants differ much one from the other.

"But it does not thence follow that the nutritive juices differ whilst in the earth, and before they have been modified by the organs of the plants. When we reflect that plants rob one another of nourishment by the roots they extend in the earth, we are even obliged to admit that the first nutritive juices are homogeneous.

"It might indeed be said, that as water enters largely into the composition of sap proper for all plants, and as it is, at least, a vehicle necessary to dissolve the other constituent parts of the sap; this vehicle, necessary to all plants, being absorbed by them, the plants must, of course, suffer, as the other constituent parts of the sap could not any longer be divided and dissolved as much as was necessary, to enable them to enter the plants. But something farther may be added; if, for instance, a Lettuce required any different food from that which supplies endive with nourishment, this Lettuce planted with Endive would thrive better than if planted among other Lettuces; Experience convinces us to the contrary. It is then certain that plants of different kinds rob one another of their food; and it seems as if this extended farther than the aqueous vehicle; but it can be made evident, that the same juice, imbibed by different plants, assumes various qualities. For instance, having taken a Lemon as big as a Pea, and grafted it by the stalk on the branch of an Orange-tree, it there throve, ripened, and still preserved its quality of a Lemon, without partaking in any thing of the Orange; this incontestably proves, that the juices of the Orange-tree received a different modification on entering into the Organs of the Lemon. All grafts prove the same thing.

"Not content with thinking there were different saps for the nourishment of every plant, some would have it, that there were in every sap particular juices to form every part of the same plant, or the same fruit. What a difference is there betwixt the flesh of a Peach, the shell of its stone, the substance of its kernel, &c.? It was, therefore, thought necessary, that it should have as many particular and distinct juices for the nourishment of each part.

"It seems very probable to me, that the organs of plants so modify the sap as to give a different flavour to fruits, and form the different parts of the same fruit; for with ever so much attention, no traces can be found either of the flavour or the smell of a root, in the earth that surrounds it; and in chewing the leaves and young branches, there is often perceived a total want of any thing analogous to the flavour, or the smell of their juicy and aromatic fruits.

"Should any one ask me how the same sap can serve for the formation and nourishment of the shell of the stone, the skin of the kernel, and the flesh of a Peach, I would, in return, ask the most able Anatomist, how the Chyle, which is the sap of animals, can form the substance of the brain, the nerves, the membranes, the flesh, the bones, the nails, &c. These operations depend on a mechanism so refined and delicate, that it has escaped the researches of the most celebrated Naturalists" (DUHAMEL 1764, Vol. I, pp. 48-50).

The publications of DUHAMEL, who was a most prolific writer, include numerous works relating to agriculture and agricultural technology. He wrote upon the culture and utilization of weld, woad, madder, saffron and other crops that were employed for dyeing; upon the use of lime, potash, brine, and arsenic as fungicides; upon the use of repellents, as turpentine, for controlling insects; upon the preservation of grain from mould and insect damage by drying, for which purpose he devised special kilns; and upon the ossification of bones in the growth of animals. DUHAMEL contributed over sixty memoirs to the Transactions of the French Academy of Sciences. In one of these contributions for the year 1757 he described details of the spontaneous combustion which occurs in the case of cloth that has been soaked in oil. Mysterious fires from this cause had been attributed to incendiarism and DUHAMEL's publication did much towards removing the unjust suspicions which sometimes result from occurrences of this kind.

DUHAMEL (like his celebrated American contemporary BENJAMIN FRANKLIN whom he so greatly resembled in versatility, practical wisdom and inventiveness) deserves to rank among the few universal geniuses of the world. By his devotion to the welfare of humanity he conferred services which place him among the great benefactors of mankind.

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Andreas Sigismund Marggraf (1709-82):— One of the most celebrated adherents of the phlogistic school was the German chemist, A. S. MARGGRAF. His father was a Berlin pharmacist under whom the son acquired his first training in chemistry. He obtained a wide knowledge and practical experience in different branches of the science by later studies at the universities of Frankfurt am Oder, Strassburg, and Halle and the mining school of Freiberg. He then returned to Berlin where as director and chemist of the Prussian Academy of Sciences he conducted chemical researches until his death.

The services of MARGGRAF to agricultural chemistry consist partly in his improvements in methods of analysis but more particularly in his important discovery of sucrose in the beet—a discovery to which the vast beet-sugar industry of the world owes its origin. MARGGRAF thus described the process which he used in first isolating sucrose from beet roots. The passage selected for translation is taken from his paper entitled,

"Chymical Experiments upon extracting a true Sugar from different Plants that grow in our Country. . . ."

"I took eight ounces of the cut chips of white mangel-wurzels, which had been carefully dried at a gentle heat, and ground them in a mortar to a coarse powder which I again gently dried as the material was somewhat hygroscopic. Of this ground and

dried powder, while it was still warm, I put eight ounces into a narrow necked flask, poured upon it sixteen ounces of highly rectified spirits of wine (which would ignite gun-powder) until the flask was half filled, and then placed it, after closing the opening with a cork, on a sand bath, where the spirits of wine were brought to boiling. The flask was then removed and its entire contents emptied as quickly as possible into a linen bag. The solution was then removed from the roots by strong pressure, filtered while still warm and then poured into a narrow necked flask with a flat bottom. After closing the flask with a cork I placed it in a moderately warm place when the solution finally became turbid. After several weeks there separated out a beautiful hard crystalline salt which had all the properties of sugar and which by redissolving in spirits of wine and recrystallizing I could obtain in a more highly purified condition. In this way sugar can be obtained from the tissues of all those plants in which its presence is suspected. . . . From a half pound of dried, white mangel-wurzels I thus obtained a half ounce of pure sugar" (MARGGRAF 1767, Part 2, pp. 73-4).

In addition to his classic work upon beet sugar MARGGRAF confirmed the disputed discovery of DUHAMEL that the basic constituent of common salt is a true alkali, different from vegetable alkali (*i.e.*, potash) and the alkaline earths (*loc. cit.*, 1768, Part I, p. 158). He also cleared up the confusion which existed as to the identity of alumina, magnesia, and lime. Another service which he rendered was his introduction of the microscope as an aid in chemical analysis. Although a most acute observer MARGGRAF always remained a firm supporter of the phlogistic doctrine. This and other errors, such as his belief in the transmutability of water into mineral substances, were common, however, to the age in which he lived and detract in no wise from the value of his accomplishments.

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Francis Home (1719-1813):— It was the incentive of a gold medal offered in 1756 by the Edinburgh Society of Scotland for the best dissertation on "Vegetation and the Principles of Agriculture" that induced FRANCIS HOME to publish in 1757 his "Principles of Agriculture and Vegetation" (the *editio princeps* of all subsequent works on agricultural chemistry). A second edition of this work was published in 1759; a third edition was printed at London in 1762 and a later one in 1776. A French translation was issued at Paris in 1761 and German translations appeared in 1762 and 1779.

HOME was born in 1719, the son of an advocate, and began the study of medicine at Edinburgh University. From 1742 to 1748 he was an army surgeon in Flanders during the Seven Years War and in the intervals of the campaign studied at the University of Leyden. After his return to Scotland he obtained his medical degree at Edinburgh in 1750, became a fellow of the Edinburgh College of Physicians and began the practice of medicine. In 1768 he was appointed professor of *Materia Medica* at Edinburgh and continued in this office until his retirement in 1798.

HOME's purpose in devoting his book exclusively to a discussion of the applications of the new science of chemistry to the ancient art of agriculture is well set forth in his introduction:—

"The principles of all external arts must be deduced from mechanics or chymistry, or both together. Agriculture is in the last class; and though it depends very much on the powers of machinery, yet I'll venture to affirm, that it has a greater dependence on

chymistry. Without a knowledge in the latter science, its principles can never be settled. As this science is but of late invention and has not been cultivated with that regard to utility and the improvement of trades and manufactures, as it ought and might, agriculture is hardly sensible of its dependence on it. The design of the following sheets is to make this appear; and to try how far chymistry will go in settling the principles of agriculture" (HOME, 3rd Ed., pp. 4-5).

Plant-nutrition according to HOME is the central dominating fact in all agriculture: —

"Let us try," he writes, "to find some fixed point from which we may have a full view of this extensive art, and from which we may proceed, in a methodical manner, to the division of our subject. All organized bodies receive their increase from the reception and application of certain particles which are designed by the Author of nature for their nourishment. Without these nutritive particles there could be no increase. As plants belong to the class of organized bodies, they thrive in proportion to the quantity of nourishment they receive at their roots. Hence arises a simple, but very comprehensive, view of husbandry. The whole of the art seems to centre in this point, viz. nourishing of plants" (*loc. cit.*, p. 6).

With the nourishing of plants at their roots as a starting point HOME proceeds to divide his subject matter into five parts: (1) the nature and qualities of different soils; (2) the nature and qualities of different composts; (3) the action of composts on vegetation; (4) tillage and cultivation; and (5) weeds and other impediments to the growth of crops. He does not discuss the applications of chemistry to animal nutrition or to the technical utilization of agricultural products. His demarcation of the field is strictly in accord with the classic interpretation of agriculture as field-cultivation (*agri-cultura*) and this limitation of treatment was adhered to by all writers upon the subject during the next sixty years and by many later authors even down to the present time.

HOME's "Principles of Agriculture and Vegetation" is a practical work, for its pages are filled with descriptions of experiments. In this connection HOME writes: —

"The operations of bodies are to be accounted for only from their known qualities ascertained by experiment. Reasoning on any other plan can never lead to truth. I shall not, therefore, proceed a single step without fact and experiments; and when I am not supplied with them from others, shall endeavour to make them myself. It is laborious, but it is necessary" (*loc. cit.*, pp. 7-8).

The old tradition of the four elements, earth, water, air and fire, still survives in HOME's treatise but to this ancient quaternary of the basic constituents of soils and plants HOME, following the leadership of STAHL, added oil and salt. His opinion upon the occurrence and importance of some of these components with reference to soil fertility is indicated in the following passages: —

"The reasoners on agriculture have failed, because they asserted, that plants were fed either by air, water, earth, or salt. I join, in some measure, with all these; and assert that plants are nourished by these bodies, united with two others, oil and fire in a fixed state. These six principles joined together, in my opinion, constitute the vegetable nourishment" (*loc. cit.*, pp. 130-1).

"Air active and fixed is to be had every where, if we are not at much pains to exclude it. Elementary fire is to be found in all bodies. Earth may be supplied by any soil managed with proper care. Water drops from the clouds. Oil is a natural principle of all earth, descends with the rains and snows, and is communicated to the

ground by all the vegetable and animal manures, in a sound or putrid state, as our experiments have shown. But whence the salt, the most active and therefore most necessary principle of all? We have not as yet discovered any in rich soil, nor in the manures most used, viz. lime, marl, shells, chalk, etc. This is an important question; opens up the action of almost all manures, and of rich soils; shows wherein the effect of the air consists; and therefore deserves a particular discussion" (*loc. cit.*, pp. 131-2).

While HOME confesses himself to be an advocate of no particular school of plant nutrition he lays chief stress on oil and salt. The blackness of a soil was attributed by HOME to its content of oil. In speaking of vegetable mould HOME writes:—

"It is observed of all soils, the mossy and boggy ground excepted, that the blackest are the richest. This colour gives us a strong presumption, that these soils contain much fat and oleaginous matter; for all fossil and vegetable oils, when they have a great admixture of earth, are of this colour. It is owing likewise to these oils, that all vegetable or animal substances gain a black colour when in the road to putrefaction. The unctuousity of this soil, a quality of it which is remarked by farmers, is a proof of its oleaginous nature" (*loc. cit.*, p. 13).

"But we have a certain method of knowing, whether a body contains any oleaginous particles or not, by the means of nitre melted in the fire. Nitre, though not inflammable of itself, becomes, in this situation, inflammable, or, as the chymists chuse to call it, deflagrates with bodies which contain any oily particles.

"Exp. I. Some rich mould taken up three or four inches deep from the border of a garden where no dung had ever been laid, deflagrated very much with nitre in fusion. Hence it appears, that this soil contains much oil" (*loc. cit.*, p. 14).

Many of the experimental proofs described by HOME are of a character similar to the erroneous test which he describes for oil and are illustrative of the very undeveloped state of agricultural organic analysis of that time. The terms oil, fat, oleaginous, unctuous, etc., applied here and elsewhere to soils, were used frequently by STAHL, HOME, WALLERIUS, and other writers of the phlogistic school in the sense of richness in organic matter (the old *terra pinguis* of BECHER). It gradually replaced the term sulfureous, as applied to combustible organic matter by BOYLE and his contemporaries. HOME was a good chemist in his time and probably knew that nitre deflagrated with other organic substances than oil. But the writers of that period seemed to have had in mind not always actual oil or fat but potential oil or fat, existing in the organic matter of the soil, which after saponification became soluble in water and hence available as a plant nutrient. By the aid of natural warmth and the supposed heating effect of alkalies, this attenuated hypothetical oil, with other volatilizable matter, was thought to be evaporated into the air and from thence brought down by dew or rain or snow. The odorous vapors from a fermenting dung-pile were regarded as an evidence of such volatilizations and the unaided restoration of fertility to a fallow field was held to be a proof of the fertilizing action of dew, rain, and snow. In this connection HOME remarks:—

"Dew is reckoned by farmers a great fertilizer of the earth. It arises from the perspiration of the earth, of vegetables and animals in a sound state, and their exhalations in a corrupted one. The earth retaining its heat, after the sun's influence is weakened, elevates these attenuated particles: but the air cooling sooner than the earth, from its rarity, condenses them at a little distance from the surface: and those which become specifically heavier than the air, fall on the earth again. Hence dew must differ according to the difference of the bodies from which it proceeds. Its contents are therefore various; but experiments have discovered, that it is composed in general

of oils, salts, and a great proportion of water. . . . Rain water, especially in the spring has nearly the same contents. MARGGRAF, in the *Academ. de Berlin*, Vol. 7, has analyzed it with great accuracy, and showed that it contains a nitrous and a sea-salt, with a considerable quantity of an absorbent earth; which probably was united to a nitrous acid before evaporation, and consequently increased the quantity of nitrous salt very much. The salts were of a brown colour, which discovered its oil. . . . Snow is justly reckoned amongst those bodies which fructify earth. . . . Both rain and snow-water putrefy sooner than spring water; which shows that they contain more oily particles than it does" (*loc. cit.*, pp. 43-5).

The same rich mould, on which he had made the deflagration test with nitre, was subjected by HOME to another examination: —

"To discover if this earth contained any absorbent or alkaline particles, I tried the following experiment.

"Exp. 2. Some strong vinegar, diluted with twice its quantity of water, being poured on this fat earth, raised a gentle fermentation, from whence many air-bubbles arose: the acid taste was at least destroyed, and the vinegar reduced to a neutral body. From this experiment we learn that rich mould contains many particles which attract acids, and with them make a neutral salt. I have learned from many different trials, that all soils fit for the nourishment of plants, contain more or less of these antacid particles" (*loc. cit.*, pp. 14-5).

These antacid particles not only play an important rôle in eliminating injurious acids of the soil but, according to HOME, perform another important rôle by the formation of beneficial salts.

"Experiments have shown", he writes, "that all fertile soils and all manures, except those already converted into mucilaginous nature, consist of particles, which in part, or all together, attract acids. Dung, the ashes of vegetables, burnt earth, contain such particles; lime, marl, animal shell, chalk, etc., are wholly of this nature. These then must attract and retain all acids, when they come within the sphere of their attraction. If the air, to which the soil is continually exposed, contains any acids, these bodies will draw it out and be converted to a neutral saline substance, enjoying the properties of salt, such as solubility in water, dissolving oils and rendering them miscible with water. Nothing then remains to be proved, in order to the conversion of these manures into a salt, but that the air contains an acid salt" (*loc. cit.*, pp. 132-3).

The supposition that the salts of the soil owe their origin to the fixation of atmospheric acids by naturally occurring acid-attractant materials is the basis of HOME's explanation of nitrate formation to which he devotes 24 pages (pp. 133-57) of his book. His arguments are interesting as an illustration of the early views upon the genesis of nitre in the soil and of its importance to agriculture.

"There are various opinions about this salt"; writes HOME, "nor are chymists yet agreed about its birth. Some alledge it is attracted, as we see it, from the air; others, that it is produced from the animals and vegetables, or their juices mixed with the nitrous earth, and putrefying there; others, that it is formed from the vitriolic acid, joining to the phlogiston, or inflammable matter of these substances: and others, that the acid of nitre is a different acid from the former, and attracted by these bodies, which are its proper matrix" (*loc. cit.*, pp. 136-7).

After discussing these various theories of nitrate formation HOME comes to the conclusion

"That the nitrous acid exists in the air, and is attracted from it. This opinion, though scarcely maintained by any chymist, to me appears to be the strongest, though still liable to some objections. The first argument for it is, That alkaline salt and

calcarious bodies of themselves, without a mixture of any vegetable or animal matter, will produce nitre; as we find by an experiment of STAHL, in which he got nitre by exposing alkaline salts to the air. I have got a nitrous salt from the lime taken out of park-walls. The second is, That it is actually found existing in nature. Many mineral waters contain a nitrous salt. . . . Thirdly, by boiling hard water, or exposing it to a great degree of heat, the nitrous acid is really volatilized, and the absorbent earth falls to the bottom. This proves, that the nitrous acid is volatile, and exists in the air. The *spiritus nitri fumans* is continually evaporating in the air" (*loc. cit.*, pp. 142-3).

For binding the spirit of nitre existing in the air HOME remarks: —

"All earths are not fit for this purpose; only such as are attracters of acids, or absorbent earths, viz. lime, marl and other absorbents; or putrefied vegetables and animals, which afford an absorbent earth, and likewise a volatile salt. Almost all earths have more or less of absorbent particles in their composition. These absorbent earths catch the nitrous acid, as it passes by them with the air, or fix and collect it as it arises from the inner parts of the earth" (*loc. cit.*, pp. 143-4).

The function of decaying plant and animal matter in nitre production, according to HOME, was a purely mechanical one: —

"The mixture of urine, and of putrefying vegetable and animal substances, will be of considerable use in carrying on an intestine motion in the mass of earth, keeping it open, and allowing the influence of the air to penetrate deeper into the body. If there was no such putrescent body mixed with it, the mass would cohere too firmly together, and its surface would only act; whereas now the whole body acts. It is in this way I imagine the animal and vegetable substances chiefly operate and not by entering into the composition of the nitre, as most chymists assert" (*loc. cit.*, pp. 144-5).

It is to this opening and exposing of the soil to the better penetration of air that HOME attributed the benefit of fine tillage, so widely promulgated by the celebrated English agricultural reformer, JETHRO TULL, and not, as TULL supposed, to the production of minute earthy particles which could be more readily assimilated by crops. In this connection HOME remarks: —

"Others think that the more terrene particles are those which nourish plants. Of this opinion is the famous TULL: because, says he, earth augments them; and whatsoever augments them, must be their food. Dung, and other manures, act only by fermenting and so attenuating the soil; and are of no more use, than, as a knife to divide their food. But earth alone could never do, without some more active principles. Had TULL been a chymist, he would have known that mere earth makes but a small part of all plants. Soil may certainly be too loose. To earth already sufficiently attenuated, manures would do no service. Whence the salts and oils of plants? These are objections which the favourers of his system never can answer" (*loc. cit.*, p. 128).

It seems strange that HOME in his long discussion of the origin of the salts in plants makes no reference to the prevalent opinion, held by WAL-LERIUS and others, that the salts of plants were produced within the vegetating organism by the transmutation of water. That HOME was not wholly adverse to highly imaginative explanations is evident from the comments which he makes regarding the supposed vegetative power of salts. He asks

"But how shall we account for the different external forms of plants? Shall we fly to the immediate hand of the Supreme Being? or, as this ought to be the last step in philosophy, can we find no chymical agents capable of this effect? From many experiments, which shew the natural inherent power in salts, especially the nitrous kind, to run into vegetations, as they are called, and to take the figure of plants, with branches, leaves, nay even an appearance of fruit, owing to the strong attachment subsisting be-

tween them and water, I have often been led to think, that the vegetable power of plants, nay their particular forms of vegetation, were owing to that vegetative power inherent in their salts. In effect, we see that vegetative power strongest when most salt enters their vessels; that is to say, in the spring" (*loc. cit.*, pp. 180-1).

This conception of HOME has some resemblance on the one hand to the mechanistic hypothesis of GREW, that chain-like combinations of different salt crystals may constitute the skeleton of plant structures, and to DUCHESNE's mystical doctrine of the palingenesis of plants from their salts on the other.

HOME discusses in general terms the properties of rich black soil, clay soil, sandy soil, chalky soil, mossy soil or peat and a variety of barren soil called till. From his experiments on a sample of the latter HOME concluded

"that this species of till contained neither salts nor oils, but was a composition of earth and iron. The poisonous quality of this soil must then have depended on the latter body. . . . Though the admixture of iron with the soil may be a very general cause of unfruitfulness, yet it seems not to be the only one. A great deficiency in some of the principles necessary for vegetation, must have the same effect. Thus farmers often give the name of till to indurated clays, and particularly to those which they find below the soil. The common farmer is afraid of stirring it up with the plow, because it is unfruitful; but the more judicious, willing to deepen his soil, takes it up by little and little, and finds that lime, dung, and air, readily fertilize it" (*loc. cit.*, pp. 34-6).

Manures were divided by HOME into three classes: (1) the fossil or mineral manures, such as marl, lime-stone, chalk, quick-lime, etc.; (2) the vegetable manures, or all plant materials, including the dung of herbivora and plant ashes; (3) the animal manures, such as calcareous shells, horn shavings, woolen rags, urine, etc. Chief attention is given to marl and to vegetable composts.

Marl (pp. 49-67), according to the analyses of HOME, is a body composed of lime and clay in different proportions, but generally about one fourth of lime and three fourths of clay. It disintegrates to a powder on contact with water, effervesces with acids and strongly attracts all oils. HOME attributes its fertilizing value to the fact that

"it will attract and fix the oils which it meets with in the ground, which fall with the snow and rain; and even those which, floating in the air, touch its surface" (*loc. cit.*, p. 54).

With regard to the application of quick-lime to soils HOME concludes from its strong saponifying action that

"it must, therefore, attract the oils powerfully from the air and earth, dissolve them, and render them miscible with water; it must, from this reason, soon exhaust the soil of all its oleaginous particles, if the farmer does not take care to supply them by dung or animal substances. Farmers have by experience discovered it to be a great impoverisher of lands" (*loc. cit.*, p. 69).

In his long discussion of dung (pp. 75-89), HOME devotes much attention to the chemistry of putrefaction, wherein he seems to have been largely guided by STAHL and the views expressed by BOERHAAVE in his "New Method of Chemistry", the third English edition of which by PETER SHAW was published only four years before the appearance of HOME's book. A few extracts from HOME are quoted:—

"Putrefaction is defined by chymists to be an intestine motion of a body whereby the union, texture, colour, smell and taste are destroyed" (*loc. cit.*, p. 75).

"Next to the excrements, which are already in a state of high putrefaction, the blood is the most putrescible fluid in the whole body; then the urine; and afterwards the solids. There are three circumstances necessary to the process of putrefaction, viz. moisture, heat, and the admission of the external air. Moisture is necessary to soften the fibres of plants, that they may be capable of the intestine motion; for we see that dry straw will not corrupt. Heat is likewise necessary, in order to excite and promote that internal motion of the particles which constitutes putrefaction. As cold checks this motion, it is a great enemy to all corruption. The admission of the external air is likewise necessary, as no intestine motion can begin without its assistance" (*loc. cit.*, pp. 76-7).

"The particular seat or subject of corruption, seems to be in the mucilaginous or oily particles; for the more of these fat oily particles a body has, it corrupts, *ceteris paribus*, the easier. Thus water, replete with the mucilaginous particles of an oozy fat soil, corrupts sooner than water taken from a gravelly soil.

"The natural progress of putrefaction in vegetables is in this way. They begin first to heat towards the centre; and emit a sharp acid smell, which is owing to the acetous fermentation. As the heat advances, this smell goes off, and is succeeded by a very foetid one. Their colour, if it was light before, now turns dark; and the more the putrefaction advances, the darker is always the colour. They lose their peculiar distinguishing taste, and gain a nauseous cadaverous one. Their fibres, which had a certain degree of firmness, lose that very soon; there is no more cohesion betwixt the minute particles of which they were composed, and they fall into a putrid pulp. These are the general circumstances which attend putrefaction.

"If vegetables are examined chymically after putrefaction, they afford principles very different from what they did before it. Their salts, which were before fixed, are now become volatile, and their oils are much more volatile and foetid than what they were. The foetid smell of putrefied bodies is owing to these volatile foetid oils flying continually off. This greater volatility in the salts and oils arises from their being more attenuated than what they were.

"How nature brings about these great changes, is difficult to say. The most plausible and general theory is, that the minute particles of air, of which there is great plenty inclosed in all bodies, extricating themselves from the fibres of the vegetable, which is now softened by moisture, and being agitated by the heat and continual alterations in the pressure of the atmosphere, raise an intestine motion in the body. This intestine motion, causing a continual friction betwixt the salts, oils, water, and earthy particles of the plant, must comminute them, and raise a great degree of heat. The oily particles undergo a change from this heat, and acquire a foetor; and, being joined by the air coming from the putrefied mass, become more volatile, and affect the sense of smelling. The intestine motion, it is easy to perceive, must take away all cohesion in the fibres and particles; and so they fall into a pulpy substance. The oils and salts having a natural affinity, will unite; and so the salts, by the natural volatility of the oil, will become volatile themselves, from being fixed before" (*loc. cit.*, pp. 77-80).

HOMÉ as a true phlogistonist believed the first mover in the putrefaction "to be that elementary fire which is inclosed in all bodies, set in motion by the external heat of the atmosphere" (*loc. cit.*, p. 81), and so it was but natural that he should also adopt STAHL's theory of putrefaction as an intestinal motion (*motus intestinus*). He quotes STAHL as follows:—

"A body in active putrefaction communicates corruption most easily to another body free from putrefaction; because being itself already in a state of intestinal motion it can easily induce the same intestinal motion in a quiescent body that is similarly inclined" (*loc. cit.*, p. 88).

It is for this reason, continues HOMÉ, that

"animal substances already putrefied, such as stale urine, human dung, the carcasses of animals, etc., are the proper putrid ferments. If the urine of horses, and stall-fed

cattle, is carried into proper reservoirs, and there allowed to turn stale, it will, if thrown on the dunghill, very much quicken the fermentation" (*loc. cit.*, p. 88).

To prevent loss of plant food from leaching of dung by rain HOME recommends that manure piles be placed in a hollow situation where the bottom is clay or paved, and which is shaded by trees to prevent the sun and wind from exhaling the volatile salts and oils. North and east winds, however, might have free access to the dung-pile, especially in winter, as these winds, according to HOME, are found by experience to be more heavily impregnated with aerial nourishment at this season than other winds. There is much visionary speculation in HOME's discussions of the care of manure and of the chemical reactions that take place in a dung-pile—subjects that are still among the most debatable in the whole field of agricultural chemistry.

In his discussion of putrefaction HOME had a dim perception of a circulation and balance of elements in the operations of nature, but, without the slightest knowledge of the photosynthetic process by which this balance is regulated, he could only indulge in idle conjectures. After confessing that "it is difficult to arrive at any degree of certainty in these obtruse speculations" he had recourse finally to the treacherous argument of design which he had previously stated should be the last step in philosophy.

"The design and end of this process", he writes, "is more apparent than the means which the Author of nature takes to accomplish these. Were vegetables to be destroyed only by external force, by far the greatest part of them would remain untouched; and so be an useless burthen on nature. Were they to be destroyed by an internal fermentation, as at present, without having their parts volatilized, the particles to which they must be reduced, would be continually washed off from the soil, carried into the sea, and so be of little use towards the nourishment of other plants. The only proper and wise scheme is followed. The oils and salts, from being fixed, are volatilized, carried up into the air and descend again to fructify the earth, which was lately robbed of them. Corruption, then, is the parent of vegetation; and could be so in no other way than in the present" (*loc. cit.*, pp. 81-2).

The same appeal to final causes is again made by HOME in a summation near the end of the treatise.

"But whence these elective attractions which move the whole? Whence acquires matter the power of acting without itself? for that must be the case, unless we suppose an endless chain of material agents. Whence but from an immaterial being, who, by his order, first fixed these properties to matter, and, by his immediate will, constantly supports them in the same tenor? It is on particles too minute for human eyes, that the omnipotent hand chuses to exert itself, and on their powers to erect this beauteous system. Hence the origin of all motion, adhesion, increase, and organised matter.

"But as all individual forms were designed to be of finite duration, he established other particles with repulsive powers, and mixed the seeds of dissolution with the first rudiments of organical life. While the vessels are pervious, and the motion of the fluids subsists, the attractive overbalance the repulsive powers, and the vegetable or animal life continues. But when that motion ceases, and other circumstances concur, the repulsive become too strong for the attractive powers, dissolve the composition, and reduce the body to those particles of which it was at first made up. This is the great circle that Omniscience has marked out, and Omnipotence circumscribes itself to, for the greatest good of the whole" (*loc. cit.*, pp. 182-3).

In the final part of his book HOME, adopting a plan that was followed also later by WALLERIUS, considers briefly certain impediments of agricul-

ture and vegetation and methods for their elimination. Weeds are controlled by cultivation, and wet land is remedied by drainage. Bad seed may be the product of weak plants.

"To produce strong plants", writes HOME, "we must chuse strong seed. Grain which has been starved in meagre grounds cannot thrive. Old grain will not grow; and therefore, farmers always chuse the last year's corn. It is thought that grain will not grow when it passes the age of five years; but the time cannot be precisely fixed, for that must depend on the driness and oiliness of the seeds. All the oily seeds keep long, some of which will lie in the earth for fifteen or twenty years: Two months after the great fire in London there appeared a great crop of a species of *erysimum*, where there had been houses for a thousand years. . . . The cause of sterility in old grains seems to consist in the vessels losing that suppleness which is necessary for their extension, and filling with water; and in the contained liquor losing that guinness which is necessary for nutrition" (*loc. cit.*, pp. 191-2).

With regard to plant diseases HOME writes:—

"All organized bodies consisting of containing vessels, and contained fluids in motion, are subject to have those fluids altered, and that motion vitiated. Hence the diseases of plants. . . . The smut, which is a corruption of the grain, ought to be classed here; because it happens most to weak grain, and in rainy seasons. It may, likewise, be communicated by infection, if I may so speak; and the smut, like other contagious diseases, may be transmitted from the infected to the healthful grain. . . . This disease is prevented, in a great measure, by steeping the grain in a pickle of sea salt. This operates in two ways. It strengthens the seed, and fits it for expelling the superabundant watry juices; and, by its great weight, suspends all the faulty grain; so that none but the heaviest and strongest fall to the bottom, and are made use of" (*loc. cit.*, pp. 193-4).

Among other impediments of vegetation, such as frost, hail, insects, etc., HOME discusses plant antipathies:—

"Among the class of external accidents we may place the effects which arise from the contiguity of certain plants. There are some plants which do not thrive in the neighborhood of others. This is observed of the cabbage and cyclamens, of hemlock and rue, of reeds and fern. We have many examples of such like antipathies amongst animals. These effects seem to be produced by the effluvia which are emitted by all organized bodies" (*loc. cit.*, p. 199).

But the greatest impediment to agriculture, according to HOME, is the lack of experiments on which a rational system of husbandry can be founded and so in the last four pages of his book he appeals to the Edinburgh Society for the Improvement of Arts and Manufactures to appoint a committee whose duty shall be "to raise a spirit of experimental farming over the country."

"In order to increase the spirit of experiment-making over the country, I would propose, that this committee should have it in their power, to grant one or more honorary or lucrative premiums, to those who shall have delivered the most ingenious and useful experiments in agriculture. . . . They ought to be, not on such subjects as the farmer is naturally led by his own gain to pursue; for such he will generally follow, to the utmost of his knowledge and abilities; but on such as are not so nearly connected with gain, and make him go out of the common road" (*loc. cit.*, p. 205).

In making his appeal for the establishment of experimental farms, for non-lucrative as well as for lucrative purposes, HOME was nearly eighty years in advance of his age. Unfortunately the time was not yet ready for carrying out his most desirable suggestions. LAVOISIER established an

experimental farm at Blois some thirty years after the date of HOME's appeal but his untimely execution prevented him from making a scientific study of agriculture on the basis of his newly established chemical theories. It was not until 1834 that an experimental farm, in the modern sense of the term, was established by BOUSSINGAULT at Bechelbronn, in Alsace.

HOME's "Principles of Agriculture and Vegetation", although the earliest special treatise on agricultural chemistry, is an honest but unsuccessful attempt to establish a rational system of agriculture and plant nutrition on the basis of the highly erroneous phlogistic hypothesis of STAHL. His book, like the similar closely following volume of WALLERIUS on the "Chemical Foundations of Agriculture", is more the picture of a disappearing epoch than the forecast of a new era in agricultural science. Before advancement could be made this science had to be purged of obsolete medieval conceptions and of a hampering cumbersome terminology by which properties were regarded as concrete substances. A new approach was needed and this was soon to be supplied by the chemists of the later phlogistic period who paved the way for the chemical revolution of LAVOISIER.

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— (1762): Third edition of the above. London, A. Millar.

Johann Gottschalk Wallerius (1709-85):— The earliest of celebrated Swedish chemists to write upon the chemistry of agriculture and the first university professor to make agricultural chemistry a subject of student research was J. G. WALLERIUS who from 1750 to 1767 was professor of chemistry, mineralogy, and pharmacy at the University of Uppsala. Although living somewhat apart from the main currents of scientific thought, his various publications won for him and his university considerable prestige in other countries. The earliest publication of WALLERIUS was a dissertation "De Causa Chymificationis" (On the Cause of Chymification), published in 1733 during his medical studies at the University of Lund; later works pertained to the origin and nature of nitre and of alkaline salts. WALLERIUS, with MARGGRAF and other chemists of his time, believed in the transmutation of water into earth and several Latin dissertations of his students, upon the mutability of water and the refutation of arguments against the transmutation of water, reflect his views upon the subject. Another curious dissertation prepared under WALLERIUS relates to DUCHESNE's old doctrine of palingenesis.

The chemistry of crops and soils was of particular interest to WALLERIUS who assigned subjects of this nature to his students for dissertations. Growth requirements of plant organs, the use of steeps for promoting the germination of seeds, the chemical principles of germination, the formation of oil in plants, causes of sterility in fields, influences of salty and clayey soils on fertility and the improvement of fields, were among the subjects investigated by students under the direction of WALLERIUS. Owing to ill health WALLERIUS resigned his professorship in 1767, when he was succeeded by BERGMAN. WALLERIUS continued to maintain his interest in agriculture, even after his retirement, and in 1779 published his observations upon the agriculture of the Upland district in Sweden.

D. D.
AGRICULTURÆ
FUNDAMENTA CHEMICA,

ÅKERBRUKETS
CHEMISKA GRUNDER,

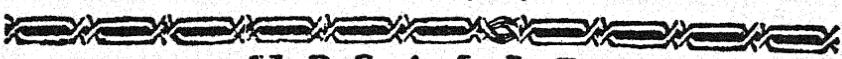
CONSENT. AMPLISS. FACULT. PHILOSOPH.
IN REGIA ACADEMIA UPSALIENSI,
PRÆSIDE,
JOHANNE GOTSCH.
WALLERIO,
PHIL. ET MEDIC. DOCTORE, CHEM. METALL. ET
PHARMAC. PROF. REG. ET ORD. ACAD. IMP. NAT.
CUR. ET REG. ACAD. HOLMENS. SOCIO.
PUBLICÆ VENTILANDA EXHIBET,
GUSTAVUS ADOLPHUS
GYLLENBORG,
COMES.
IN AUDITORIO CAR. MAJ. AD D. XXIII. MAJI
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UPSALIÆ.

FIG. 20. — Title page of the "Agriculturae Fundamenta Chemica", a doctor's thesis of Count GUSTAVUS ADOLPHUS GYLLENBORG prepared under the direction of Professor JOHANN GOTTSCHALK WALLERIUS at the University of Uppsala, 1761, and published in Latin and Swedish. The first book with a reference to the chemistry of agriculture in its title.

Of particular interest to agricultural chemists is a dissertation in Latin and Swedish prepared in 1761 under the direction of WALLERIUS by his student Count GUSTAVUS ADOLPHUS GYLLENBORG and entitled "The Chemical Foundations of Agriculture" (*Agriculturae Fundamenta Chemica: or Åkerbrukets kemiska Grunder*)*. This book of 321 pages (actually only 160 for the Latin and Swedish are on opposite pages) is the first to indicate specifically the relations of chemistry to agriculture in its title and for this reason has been wrongly considered to be the first book upon agricultural chemistry. While there is no direct evidence that WALLERIUS, whom we may consider to be speaking through his pupil GYLLENBORG, was familiar with HOME's "Principles of Agriculture and Vegetation" there is a remarkable similarity in method of treatment and in some of the views of these two writers.

WALLERIUS limits his treatment of the Chemical Foundations of Agriculture to the consideration of soils and crops, thus following HOME in his rigid adherence to the literal etymological meaning of agriculture. The following summary is given of the chapters of the book:—

Preface (pp. 1-5)

The author does not regard his subject as a separate science but only as a division of a more general science, Economic Chemistry (*Chemia Oeconomica*), which covers the general field of all rural and domestic operations (*res rurales et res domesticas*). He proposes to treat only that part of the subject which is concerned with field science, or what was later called agronomy.

The distinction which is drawn shows an early appreciation of the great complexity of the field of rural science and of a desire to limit the discussion to what the author considers to be the true chemical fundamentals of agriculture:—

Chapter 1. The Composition of Plants (pp. 6-34)

All plants of whatsoever kind when analyzed chemically, without the use of fire, are found to contain (1) unctuous oils; (2) essential salts; (3) mucilaginous juices; (4) gummy juices; (5) saponaceous juices; (6) resins, resinous and buttery juices; (7) certain gaseous ingredients; (8) odorous spirits. When plants are examined chemically by use of fire, they yield (1) water; (2) acid and alkaline salts which are generally fixed, rarely volatile; (3) essential and empyreumatic oils; (4) earth, which is either vitrifiable, absorbent, or calcareous.

It will be noted that this classification of plant constituents shows little advancement over that proposed by PARACELSUS two centuries earlier.

Chapter 2. The Principles of Plant Growth in General (pp. 34-48)

By the principles of plant growth we mean not only those constituent materials, whether compound or mixed, that enter the composition of plants and so promote plant growth (*nutritiva*) but also those which assist such growth by an activating influence

* WALLERIUS is usually, and no doubt justly, accredited as author of the work, although in a flattering addendum on the last page of the dissertation WALLERIUS mentions the book as an evidence of GYLLENBORG's diligence in the sciences that are most useful to the public welfare. GYLLENBORG in the dedication of his dissertation to Crown Prince GUSTAV of Sweden describes it as the first fruits of his learning. Under present rules of cataloging it is customary in case of dissertations published at European Universities before 1800 to attribute authorship to the professor and not to the respondent. It is supposed that many Latin theses of this period, especially of students of the nobility, were written entirely by the professor.

(*instrumentalia*). Plant nutrients to be absorbed must be exceedingly fine, or liquid, or gaseous (*vaporosa*). Pinguefaction (i.e. making the soil fat) is the basis of nearly all agriculture. Nutrition is not promoted by heterogeneous but by homogeneous substances. Plants derive no growth from any mineral earth or from substances of a sulphurous, bituminous, stoney or metallic nature since these are of a different nature from that of plants. The substances that promote plant growth must be (1) identical or analagous with substances preexisting in the plant, or (2) capable of being transmuted and combined into a nature that belongs to plants.

The terms fat, fatty, etc., applied here and elsewhere to soils, were used in the same sense as employed by STAHL, HOME, and other writers of the early phlogistic school:—

Chapter 3. The Intrinsic Multiplicative Power of Seeds (pp. 48-72)

Ripe seeds of plants when subjected to chemical examination yield no saline matter on leaching with pure water. On distillation they yield an oily acid spirit and then oil, with a residue of earth. Heated on an open fire they give off smoke, carbonize, and, when all oily and volatile matter is expelled, leave a small residue of white vitrifiable earth. The smaller the amount of this earth, the more nutritious is the seed from which it was derived. This earth is transmuted from water by an intrinsic motion and is combined with a considerable quantity of oil reduced to a more solid earthy consistency. Experiments show that water can be transmuted into vitrifiable earth and that oils can be transmuted into inflammable earth.

The belief, which WALLERIUS expresses in the transmutation of water into mineral matter by the vital activity of plants, was very commonly held by chemists and plant physiologists of his time and it was not entirely dispelled until over 50 years after his death. Relics of the old belief in a quaternary of elements appear in the following chapters devoted to heat, air, water, and earth, as they did in the treatise of HOME:—

Chapter 4. Heat as a Promoter of Plant Growth (pp. 72-84)

Heat operates on plants actively in promoting the movement of their humors, on which nutrition and reproduction depend, and in activating their vital intrinsic principle. Heat operates also in a material way by contributing to the nutritive inflammable matter of plants. It is shown in Physical Chemistry that heat consists in the motion of a calorific matter. An excess of heat as well as a deficiency is harmful to the growth of plants.

Although he does not employ the term, WALLERIUS was a consistent follower of STAHL's phlogistic school of chemistry, as was also HOME:—

Chapter 5. Air as a Promoter of Plant Growth (pp. 84-110)

The air which is so necessary for the life of plants and animals contains many particles that are either exhaled or transformed into air. Among these are mentioned: (1) water, vaporized from the sea, lakes, rivers, etc.; (2) volatilized inflammable substances on which all the heat existing in the air depends; (3) oils and fats, volatilized by the action of heat; (4) saline substances such as the more delicate acids and volatile alkalies. Those who argue that nitre, sulphur, or other solid saline or sulphurous particles are in the air, are completely deluded, since bodies of this kind cannot be vaporized. In addition to the air and its various exhalations there is present in our atmosphere a certain nutritive revivifying principle by which the growth of plants and the life of animals are sustained. This is the so-called hidden food of life (*occultum vitae pabulum*) variously termed nocturnal dew, defluent life, rarefied water, etc. It is this occult principle which restores fertility to fallow fields.

In his advocacy of an occult food of life, WALLERIUS is repeating the speculations of PALISSY concerning "generative water" in 1580 and of

BOERHAAVE concerning the "aura", or "spiritus rector", in 1753. It corresponds also with SPRENGEL's conception of "life atoms" promulgated in 1830, 69 years after the publication of WALLERIUS' book. These mystical vitalistic ideas have continued to reappear throughout the whole history of agricultural chemistry.

Chapter 6. Water as a Promotor of Plant Growth (pp. 110-134)

The dictum that "plants cannot grow without water" can be amplified to read "plants can grow with water alone". That earth contributes nothing to the growth of plants was proved first by VAN HELMONT and after him by BOYLE. A review of all experiments proves that earth although serving as a firm support for plants is not carried into them with water, but that the water existing in plants is by its own motion transmuted into earth. Water can be transmuted into salt and oil with the aid of heat or putrefaction. Water acts beneficially on plants in two ways: (1) materially by serving as a nutrient; (2) instrumentally by softening plant tissues to facilitate growth, by promoting the fermentation excited by warmth and air, by acting as a menstruum for saline and nutrient particles and by serving as a vehicle for removing excreta and superfluous dregs. Water must be supplied to fields in the right amount. An excess is injurious as well as a deficit. We cannot conclude that the more abundant supply of a nutrient will result in a more abundant crop (*ab uberiori alimenti copia, non possumus concludere ad uberiorem messem*).

In this chapter as elsewhere WALLERIUS clings tenaciously to the old idea that water can be transmuted by vital forces into all the mineral and organic substances required for the sustenance and growth of plants. He mentions the experiments of WOODWARD but fails to realize their significance. Yet in the midst of his fallacies the reader discovers many sage observations. His remark that more nutrient does not necessarily result in a greater crop is a foreshadowing of what was later known as the law of diminishing returns.

Chapter 7. Earth as a Promoter of Plant Growth (pp. 134-9)

The view is erroneous that crops are nourished by assimilating minute particles of earth, because (1) of the different nature of vegetable earth as totally distinct from any kind of mineral earth, because (2) of the insolubility of any kind of earth in water, without which solution earth cannot be translocated, still less penetrate the absorptive vessels (of plants) and because (3) of experiments which have been conducted, we conclude that no vegetable food can be obtained from earth as such. This nullifies the chief axiom of JETHRO TULL, of DUHAMEL DU MONCEAU (*Traité de la culture des terres, suivant les principes de M. TULL*) and of others who believe earth to be the principal nutriment of vegetables.

Chapter 8. Humus as a Promoter of Plant Growth (pp. 140-152)

Humus is an earth more or less spread out and disintegrated on the surface of the ground and of very dark color. When water is added it swells up immensely to a spongy mass which on drying greatly contracts to a powdery condition. It gives up water easily by translocation and evaporation. When the extract, obtained by leaching humus at a mild heat, is evaporated it leaves a light yellow powder with a salty taste. With a stronger heat the liquid extract is dark; this when concentrated has a sharp odor and taste; if evaporated to dryness it yields a salty glutinous residue soluble in water. The salty substance, obtained from humus by leaching, consists sometimes of an alkaline matter, sometimes of *sal mirabile*, sometimes of nitre, sometimes of other ingredients; *sal muriaticum* is always present. All these salts must then be regarded as accidental constituents of humus. Humus yields on distillation (1) more or less phlegm, depending on whether the earth is more or less dry; (2) a volatile spirit, sharp and empyreumatic, of dark color, not unlike spirit of tartar; (3) a reddish oil.

From this it appears that humus is derived from decomposed plants since no glutinous, nor spirituous, nor oily matter of this kind is found in the mineral kingdom. Humus is most useful when mixed with a clayey land, as it renders this more soluble. Those who argue that humus is converted into clay seem to be ignorant of the true nature of humus and clay. Humus is of chief value in promoting plant growth (1) materially by supplying fatness for nutriment, and saltiness, by the aid of which the fat can be mixed with water. These are quickly separated by water and heat, which is prevented when clay is mixed therewith; (2) instrumentally by attracting and retaining the fatness present in the air which is bound more strongly by homogenous bodies; (3) owing to its porosity and solubility air is admitted to germinating seeds and to the roots of the same without which activity plants can scarcely grow; (4) cultivation is made easy.

The definition and description of humus given by WALLERIUS became current and they can still be accepted with some minor reservations. His ideas on the value of humus as a plant nutrient coincide with those held later by THAER, BERZELIUS, MULDER and other advocates of the theory that was so vigorously contested in 1840 by LIEBIG. The resemblance, here and elsewhere, between the ideas of HOME and WALLERIUS about the retention by soils of areal fatness is at once apparent.

Chapter 9. Clay as a Contributor to Fertility (pp. 152-164)

Clay is a tenacious earth, fatty to the touch, thick, dense, sticking to the fingers when moistened, and composed uniformly of exceedingly minute particles. As distributed on the surface of the ground it is most usually mixed either with humus or with sand or with other heterogeneous particles, whence it differs more or less in tenacity and other properties. It not only attracts and holds water but when mixed with it forms a tenacious paste. It transmits water scarcely at all and loses it only by evaporation; it thus becomes the principal means of conserving subterranean moisture. Subjected to distillation clay yields: (1) phlegm which, however, differs greatly, being found pure by some, of a urinous character by others and of a somewhat acid nature by others; (2) a certain amount of a sublimed salt of an ammoniacal or urinous character. Oil and fat cannot be obtained from clay either by leaching or by distillation. Clay contributes to fertility not materially since it contains no fatness, but instrumentally by attracting and collecting water and subterranean vapors and protecting them from evaporation longer than any other earth; and by retaining the fatty and areal particles that originate from dung or other material, whether added or otherwise present, so that they cannot be dissolved and carried away by rain water. Clay can act detrimentally owing to its stickiness and tenacity. It releases moisture and fat with difficulty, keeps air from germinating seeds and roots, and by its dampness resists the action of heat, for which reason farmers call it "cold earth". Clay is softened by an excess of water and sticks to the plow; afterwards when it dries it hardens into big clods. When water fails it becomes harder and can scarcely be broken up by the plow. For these reasons it is evident that no plants, or very few at least, can grow in pure clay.

Chapter 10. Chalk and Lime as Contributors to Fertility (pp. 164-176)

Chalk and lime absorb added water and give it up quickly. Extraction with water dissolves a little chalk and lime with production of lime-water which effervesces with acids and has a great power of decomposing fatty and sulphurous substances. Chalk and lime effervesce with acids and neutralize their acidity. When the mixture is distilled the residue can scarcely be brought to dryness owing to its very strong hygroscopic power. Chalk and lime have a great power of decomposing fats and oils, especially in presence of water and heat. They contain no fatness and so supply no nutriment directly to plants but they are of great benefit instrumentally by attracting an acid fatty principle from the air, by supplying warmth to field and water, by assisting germination, by eliminating soil acidity, by dissolving the unctuous matter of a field and rendering it more miscible with water, by facilitating cultivation and by cur-

ing smut which is not caused by insects but by the corrosive action of the oily part of seeds by which they are burned as if by fire. Chalk and lime have certain disadvantages among which are (1) attracting too much heat by which the seeds and roots of plants are burned; (2) hardening the coats of seeds so that entrance of nutrients is prevented; (3) liberating and consuming the fatty richness of fields too quickly, whence the saying "Only old men are enriched by fertilizing fields with lime".

In this chapter WALLERIUS clings to the old tradition, contested two centuries earlier by PALISSY, that calcareous manures have a persistent heating effect on soils. His mention of lime as a cure for smut is an early reference to its use as a fungicide. In referring to the benefit of lime for eliminating soil acidity WALLERIUS stumbles upon a truth in his blind efforts to explain long established agricultural practices.

Chapter 11. Marl as a Contributor to Fertility (pp. 176-184)

Marl is a mixture of clay with calcareous earth and therefore shares the nature of each of them. Every marl, when mixed with water, disintegrates and, no matter how hard when excavated, sooner or later by action of the air is reduced almost to a powder. In common with clay it retains moisture but to a less degree. Nothing salty or fatty can be obtained from marl either by extraction or distillation. After cooking with water the filtered extract does not change the color of sirup of violets. Every marl effervesces with acid. Marl does not nourish crops directly since it contains no fatty matter and no fertilizing salt, but indirectly is most beneficial by removing soil acidity, by converting the fatty matter of the soil into a soapy water-soluble mixture which can enter the pores of plants and by diminishing the cohesion of clayey particles which are thus made more easy of cultivation.

Chapter 12. Sandy and Gravelly Earths as Contributors to Fertility (pp. 184-190)

Sand and gravel are of no nutritional benefit to plants either directly or indirectly. They may be of some incidental service in mixture with tenacious soils by rendering them more porous and easier to cultivate and by permitting air to have readier access to the roots of plants.

Chapter 13. Salts as Promoters of Plant Growth (pp. 190-213)

Although many writers assert that salts are the sole cause of fertility, our own opinion is that salts of any kind cannot of themselves promote plant growth. We have never been able to extract the slightest trace of salts from cereals. Many who have tried to fertilize a field by sprinkling it with sea-salt were unable to grow anything on it thereafter for many years. Common salt, however, if used sparingly, has an indirect benefit in attenuating and dissolving the fatty nutrients of a soil. MAYOW, GLAUBER, BACON and others claimed nitre to be the sole cause of plant growth, giving as arguments: (1) that it was praised by the ancients; (2) that it is everywhere present in the air; (3) that it occurs in plants, although is changed on burning them into alkaline salt; (4) that its fructifying power has been proved by experiments, dung itself being changed to nitrous earth before producing its maximum fertilizing effect. These arguments, however are unreliable, because: (1) the nitre of the ancients was natron or mineral alkali; (2) nitre and other salts do not occur in the air but only their acid principles; (3) nitre occurs in plants only rarely. The alkali salt formed in burning plants is not derived from nitre but from earthy, or other essential, salts; (4) we grant that dung on putrefaction is converted into nitrous earth which, however, does not supply nutriment directly but only indirectly by the action of nitrous salt in rendering the fatty richness of soil available to plants. We should therefore not attribute to nitre what is due to the fatness mixed therewith. Alkali salts, such as unleached wood-ashes, have been commended. They operate in the same way as lime but to a far greater degree both as regards advantages and disadvantages. Prudently used they are of most benefit to fatty soils, but if used in excess they are more injurious than other salts by dissolving away all the fatness and leaving an exhausted soil for the next crop. For this reason forests, in places that have been burned over several times, are replaced only slowly by new trees. We thus conclude that mineral salts and mineral earths are

not plant nutrients. The true nutrients are the water, inflammable matter, fatty principles and acids which plants absorb. From them plants produce by a continued process of fermentation attenuated oil or spirit which is perceived by its odor and is different in different plants. From this attenuated oil, by a process of concentration and coction, there is finally produced true oil and spirit which exist separately. This is the true method of nature who advances by gradual steps from more simple to more complicated substances in producing the constituent parts of plants.

WALLERIUS in opposition to HOME shows upon the whole a tendency to minimize the fertilizing value of salts which had been so strongly advocated by PALISSY, GLAUBER and other early writers on the subject. He was hampered here as in other respects by the mistaken belief that plants could create their own mineral requirements by the transmutation of water.

Chapter 14. The Art of Promoting the Multiplicative Power of Seeds (pp. 214-252)

The use of nurseries for developing select seeds of high productivity has much to recommend it, but soil and climate must also be considered as important factors. The farmer must determine whether the economic returns from the use of nurseries justify the extra labor and expense. The use of steepes for increasing the germinating power and productivity of seeds has been advocated on the ground: (1) of protection against insects, blight, smut, etc.; (2) of promoting the emergence of the germ and radicle by softening the outer skin of seeds; and (3) of conveying nutritive matter to the seed embryo. Lime, soot, garlic juice, and other substances have been used to advantage in protecting seeds against injury from worms, etc., but are useless in case of bad seed. Softening the seed coats may be beneficial but such seed is exposed to other hazards such as destruction by freezing of the imbibed water. The use of such steepes as honey, milk, wine, etc., for conveying nutriment to germinating seeds is of very doubtful benefit. Of the immersive steepes made with alkalies, nitre, oils, acids, urine, saponaceous mixtures of wood ashes with dung liquor, etc., and other fluid preparations, simple rain water is to be preferred to all these artificial concoctions. Rain water, with its content of aerial fat particles, etc., is a most excellent plant nutrient. No steep for seeds is absolutely safe under all conditions. Each has its particular hazards and must be used with caution. The dusting of seeds with lime, soot, gunpowder, etc., for promoting their multiplicative power has little advantage as these dry powders do not adhere to seeds. Soot, however, may take the place of the best dung when mixed with soil as a fertilizer owing to its content of oil, earth, salt and other ingredients homogeneous to those of plants. Soot also is beneficial owing to its retaining heat, neutralizing acid and resisting insect attacks. Soot is derived from smoke but fumigation of seeds with smoke is of doubtful value.

Chapter 15. The Manuring of Land (pp. 252-274)

Manuring (pinguefaction) is that operation by which land receives substances that nourish plants. Since neither earths nor salts supply homogeneous nutrients to plants it follows that the benefit of manure consists in supplying land with a sufficient amount of fatness and humidity. The fatty aqueous mixtures of dung must be attenuated and vaporized by putrefaction before they can be assimilated by plants. The dung of well-fed cattle, when mixed with their urine, being most easily putrefied, is therefore the best manure. Dung consists of finely chewed vegetable matter, mixed with saliva and other animal fluids, and contains fatty ingredients closely approaching the nature of vegetable oils. Its manurial value is not due to saline ingredients but depends only on its quantity of fatty matter and the solubility of the latter in water. The quantity of fatty matter in the dung is determined by distillation; it varies according to the food of the animal. The more fatty the dung, the warmer it is. The dung of fowls, who feed chiefly on seeds, is hotter than that of horses, horse dung is hotter than that of cows, and so on. The views of TULL and DUHAMEL, that dung supplies no nutriment to crops but only by its putrefaction subdivides the particles of earth and makes them thus easier to assimilate, are completely erroneous. The leaves, twigs and bark of trees, sawdust, and similar refuse contain little oil and make a compost inferior to animal manure. Dung should be spread on the land without delay and mixed with the soil as evenly as possible

in order that its fatty richness may not be lost. The quantity of manure to be used depends on the nature of the land. The wetter and colder the field, the more dung is needed to supply the necessary heat. Dung loses its effect after 5 or 6 years, even in good soils, and must then be renewed. With poor sandy soils the renewal must be made much sooner.

Chapter 16. Mixing of Soils (pp. 274-290)

A clayey soil that is too tenacious and too cold can be remedied by mixing with it a lighter, warmer sandy soil. A soil that is too acid can be corrected by adding marl, ashes, or lime. So also a soil that is too dry can be improved by the addition of a clayey, or other moisture-attracting soil. In this connection regard must be had to the differences in preference of particular crops. Mixing of soils may be performed by transporting one soil to another either directly or after enrichment with dung. It may also be accomplished in some cases by mixing a subsoil with the soil above. A barren unproductive subsoil should usually remain untouched and never be allowed to degrade a richer surface soil, although cases are known where a soil that is very barren when first turned up, afterwards, on repeated plowing, becomes very productive through attraction of fertilizing elements from the air.

Chapter 17. The Plowing, Sowing and Cultivating of Land (pp. 290-310)

Plowing is necessary to aerate the soil, to dissipate noxious acid, to eradicate weeds and to secure a better mixture of the soil with manure. Land should not be plowed when the soil is wet, lest clods be formed. The depth of furrows should equal the length of the roots of the particular crop to be planted. Seed must be covered to protect it during germination and to shelter it from birds, insects, etc. The depth of earth above seeds should not exceed six inches. With rich soils plants stool better and hence less seed is needed than on poor soils. Crusts on the soil should be broken to permit the young plant to emerge.

Chapter 18. Elimination of Some Obstacles That Beset Agriculture (pp. 310-321)

Among obstacles that impede the nutrition and growth of plants and which the industry of man can eliminate are: (1) trees, which should not grow on cultivated land as they shut off sunlight, rob crops of nutrients by their roots and smother them with fallen leaves. Leaves also acidify the soil where there is stagnant water; (2) excessive water, which should be removed by drains; (3) hillocks and huge stones, which retain snow and hinder drainage, should be disposed of; (4) crops must also be protected from animals by fences, ditches or other means.

The agricultural chemical dissertation of GYLLENBORG, sponsored and no doubt largely written by WALLERIUS, is of great historic interest. It is the earliest book with a reference to agricultural chemistry in its title; it is filled with references to the opinions of ancient and contemporary writers; and, with its use of Latin and a somewhat dialectic style, it is a late example of the medieval scholastic method of science writing, that still prevailed in many European universities. The book of WALLERIUS is the best summation that we have of the early phlogistic theories of agriculture and plant nutrition, that were soon to disappear before the demolition that was wrought by the discoveries of the later phlogistonists and of LAVOISIER.

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Chapter V

AGRICULTURAL CHEMISTRY IN THE LATE PHLOGISTON PERIOD

Joseph Black (1728-99):— For over a century after VAN HELMONT had announced the production of his *gas sylvestre* by the burning of charcoal, by the fermentation of wine and beer, and by the action of vinegar upon limestone, and after he had mentioned also its natural occurrence in caves, it failed to be suspected by chemists that this new aeriform spirit might be a constituent of the atmosphere, that it might possibly play an important rôle in plant and animal life and that it might serve as a hint that other gaseous bodies produced in their chemical experiments were substances entirely different in character from ordinary air. One reason for this oversight was that chemists were still hampered by the preconceived notion of a quaternary of elements and hence believed all gaseous substances to be identical with elemental air, although recognizing that such air might be contaminated at times with impurities.

Another explanation for the apparent slowness of the older chemists to perceive what we now think as obvious was the absence of definite chemical tests by which the character of an individual gas could be recognized. VAN HELMONT knew that his gas sylvestre asphyxiated animals and extinguished lights; CLAYTON, HALES and others knew also that some of the "airs" produced by destructive distillation were inflammable; but other more specific tests were needed before the presence of one gas in admixture with others could be detected. For this first great step in the development of pneumatic chemistry the world is indebted to JOSEPH BLACK.

BLACK, who was of Scottish descent, studied first at the University of Glasgow where he heard the chemical lectures of the famous Dr. CULLEN. Deciding to become a physician he entered the University of Edinburgh and published there in 1754 his Latin thesis "*Dissertatio de humore acido a cibo orto et de magnesia*", the chemical part of which appeared in 1755 as an English essay with the title, "Experiments upon Magnesia Alba, Quicklime and other Alkaline Substances." In this work BLACK showed that *magnesia alba* (magnesium carbonate) on being heated gave off a gas which he called "fixed air" (carbon dioxide) and that the loss in weight thus incurred was regained when the calcined *magnesia alba* was made to recombine with the gas that had been given off.

After obtaining his medical degree BLACK succeeded CULLEN as lecturer in chemistry at Glasgow. In 1766 he succeeded CULLEN again as Professor of Chemistry in Edinburgh and lectured there until his retirement in 1797. Many famous scientists were trained under BLACK among whom were several Americans, including BENJAMIN RUSH and SAMUEL LATHAM MITCHILL.

BLACK's classic researches on quicklime were begun in 1752 as part of an investigation upon its use as a remedy for urinary calculi. It was then supposed that when limestone was calcined the addition of phlogiston made it caustic. BLACK showed, however, that nothing was gained from the fire in this process but that in its conversion to quicklime the limestone lost

nearly half its weight. This loss BLACK showed to result from the escape of a particular kind of air which, from its being fixed in limestone and other substances, he called "fixed air". The account of this discovery, as described in BLACK'S "Lectures on the Elements of Chemistry" (1803 ed.), is related as follows:—

"Here a new, and perhaps boundless field seemed to open before me. We know not how many different airs may be thus contained in our atmosphere, nor what may be their separate properties. This particular kind has evidently very curious and important ones. It renders mild and salutary the most acrid and destructive substances that we know. I resolved to begin the study of them, by a closer examination of the species which I had fortunately discovered.

"I gave it the name of Fixed Air, for the reasons already mentioned, a term which was then common to denote any elastic matter, capable of entering into the composition of bodies, and of being condensed in them to a solid concrete state, by its chemical attraction for some of their constituent parts. The name may perhaps be thought to be not very judiciously chosen, to denote this matter in its elastic state: and accordingly it has now been changed for gas. But I chose rather to employ a term already familiar, than invent a new name, before I was well informed respecting the peculiar properties of this substance.

"It is somewhat singular, that when a solution of mild alkali is rendered caustic by lime, the specific gravity is considerably diminished. We should naturally expect the contrary effect, from the abstraction of so rare a fluid as air. But this shews, that in the solution the fixed air is rendered considerably denser than water, being reduced to less than $1/860$ of its aerial bulk.

"I fully intended to make this air, and some other elastic fluids which frequently occur, the subject of serious study. But my attention was then forcibly turned to other objects. A load of new official duties was then laid on me, which divided my attention among a great variety of objects. In the same year, however, in which my first account of these experiments was published, namely 1757, I had discovered that this particular kind of air, attracted by alkaline substances, is deadly to all animals that breathe it by the mouth and nostrils together; but that if the nostrils were kept shut, I was led to think that it might be breathed with safety. I found, for example, that when sparrows died in it in ten or eleven seconds, they would live in it for three or four minutes when the nostrils were shut by melted suet. And I convinced myself, that the change produced on wholesome air by breathing it, consisted chiefly, if not solely, in the conversion of part of it into fixed air. For I found, that by blowing through a pipe into lime-water, or a solution of caustic alkali, the lime was precipitated, and the alkali was rendered mild. I was partly led to these experiments by some observations of Dr. HALES, in which he says, that breathing through diaphragms of cloth dipped in alkaline solution, made the air last longer for the purposes of life.

"In the same year I found that fixed air is the chief part of the elastic matter which is formed in liquids in the vinous fermentation. VAN HELMONT had indeed said this, and it was to this that he first gave the name *gas silvestre*. It could not long be unknown to those occupied in brewing or making wines. But it was at random that he said it was the same with that of the Grotto del Cane in Italy, (but he supposed the identity, because both are deadly); for he had examined neither of them chemically, nor did he know that it was the air disengaged in the effervescence of alkaline substances with acids. I convinced myself of the fact by going to a brew-house with two phials, one filled with distilled water, and the other with lime-water. I emptied the first into a vat of wort fermenting briskly, holding the mouth of the phial close to the surface of the wort. I then poured some of the lime-water into it, shut it with my finger, and shook it. The lime-water became turbid immediately.

"VAN HELMONT says, that the *dunste*, or deadly vapour of burning charcoal, is the same *gas silvestre*: but this was also a random conjecture. He does not even say that it extinguishes flame; yet this was known to the chemists of his day. I had now the certain means of deciding the question, since, if the same, it must be fixed air. I made several indistinct experiments as soon as the conjecture occurred to my thoughts; but they were with little contrivance or accuracy. In the evening of the same day that I

discovered that it was fixed air that escaped from fermenting liquors, I made an experiment which satisfied me. Unfixing the nozzle of a pair of chamber-bellows, I put a bit of charcoal, just red hot, into the wide end of it, and then quickly putting it into its place again, I plunged the pipe to the bottom of a phial, and forced the air very slowly through the charcoal, so as to maintain its combustion, but not produce a heat too suddenly for the phial to bear. When I judged that the air of the phial was completely vitiated, I poured lime-water into it, and had the pleasure of seeing it become milky in a moment.

"I now admired VAN HELMONT's sagacity, or his fortunate conjecture; and, for some years, I took it for granted that all those vapours which extinguish flame, and are destructive of animal life, without irritating the lungs, or giving warning by their corrosive nature, are the *gas silvestre* of VAN HELMONT, or fixed air" (*loc cit.*, Vol. 2, pp. 86-8).

As BLACK correctly states VAN HELMONT had only surmised that the "airs" of vinous fermentation and of the emanations of caves were the same as his *gas silvestre*. It remained for BLACK to prove the identity of these various gases by the lime-water test and also to establish the additional highly important fact that this same gas was given off by animal respiration. Here then was a new aeriform body with definite recognizable properties, different from those of ordinary air. A powerful stimulus was thus given to the search for other new "airs", of which many were discovered in the following decades.

Results similar to those obtained with limestone were obtained by BLACK with *magnesia alba* (magnesium carbonate). He showed too that when *magnesia alba* was mixed with lime water, the "fixed air" left the magnesia and joined the lime and that when quick lime was added to solutions of the mild alkalies (*i.e.*, sodium and potassium carbonates), the same type of reaction occurred, the "fixed air" going to the lime from the alkalies which were thus rendered caustic. BLACK also proved that when quick lime is exposed to the atmosphere, it slowly attracts not the air but only the "fixed air" which is diffused therein.

BLACK's investigations upon lime led him to make an investigation of the various calcareous manures. His statements upon marl are quoted:—

"There are also some fossil earths, which, though they be not composed entirely of calcareous earth, but, on the contrary, contain sometimes but a moderate portion of it, deserve, however, to be mentioned here, on account of their usefulness and importance. These are the earths called *Marles*, which have been long successfully employed as manure to improve soil. Every substance to which the name of marle is properly applied, and which proves of general usefulness as a manure, contains more or less calcareous earth; and is useful and valuable in proportion to the quantity it contains.

"Marles are commonly divided into three kinds—*Shell Marle*, *Clay Marle*, and *Stone Marle*.

"1st, *Shell marle* is composed of the shells of shell-fish, or other crustaceous aquatic animals, lying together in immense quantities. Many are entire, but in general they are decayed, and mostly mouldered down to dust, and intermixed with more or less sand, or other earthy substances. When we examine this matter, as occurring in different places, it may be distinguished into two kinds—fresh water marle, or bog marle, and sea-shell marle. We have an example of bog marle in the Meadow, composed of the shells of the small fresh water wilk or snail, which multiply greatly in lakes or ponds, or brooks of fresh water, and of other shells, which are gradually deposited in great collections by the water. The other kind of shell marle, the sea-shell marle, constitutes much greater collections, which are found in many places, though at present far removed from the sea. One of the most noted examples has been described by Mr. REAUMUR, in the Memoirs of the Academy.

"2dly, Clay marles consist of earths of different colours, which more or less resemble, and actually contain clay; but with it some calcareous earth is mixed, in fine powder like chalk.

"3dly, Stone marles are of very great variety in colour and appearance. They are harder and more stony than clay marles, and that is the only distinction between them; but they differ from masses properly stony in this, that by being only a few weeks or months exposed to the air, they split into pieces, and crumble down into earth, or a matter like clay. Some, however, take a long time to break down in this manner; and there is all the variety possible in this respect between them and the clay marles. This disposition to moulder down by the weather, depends on the admixture of clay, which they contain. A consequence of the gradual, though very slow dissolution of this earth by water, has been observed in the strata of hard marles. It has been found by experience, that such strata do not contain any calcareous earth where they crop out, on the surface of the ground, nor even at the depth of a few feet below this. Many gentlemen who were in possession of a stratum, which they knew, from the neighborhood, to be a rich stone marle, have, without fear, expended great sums of money, and covered much of their land with this crop marle. They not only lost their money, but, in many cases, spoiled their land, by filling it with a hard baking clay. This effect upon beds of marle is without exception; and it is even found that the upper plates of single strata of limestone are deteriorated in the same way. This fact also explains, by the way, the wearing out of lime used as a manure upon land.

"When we now examine with attention many of these natural collections of this sort of earth, we are led to a conclusion which may appear surprising at the first hearing of it; but which is founded on a multitude of the most authentic facts.

"The inference I mean is, that all the large collections of calcareous earth have derived their origin from shells and lithophyta, or that they were once in that form. The proofs of this are so numerous and striking, that they cannot be resisted.

"1. Beds of sea-shells, or other calcareous productions of the sea, are found in many parts of the world, of great extent, and in all the different states of decay.

"2. We find abundance of shells, or fragments of shells, and of zoophytes, in the greatest number of the calcareous strata of marbles, limestones, and chalk; which are the greatest collections of calcareous earth.

"We do not find shells in calcareous spar, nor in stalactites; but it is evident that these forms of the calcareous earth have been completely fluid, so that all the organic structure of the original matter is necessarily lost.

"There are also many marbles and limestones, in which we do not find any of the appearances I speak of. But this too can be explained, by examining their structure or aggregation, which shews that the matter of them has been dissolved or liquefied by other operations of nature" (*loc. cit.*, Vol. 2, pp. 26-29).

Certain limestones of high magnesia content are mentioned by BLACK as producing a lime that greatly impaired the fertility of the land (*loc. cit.*, Vol. 2, p. 69). This is one of the earliest references to the toxicity of magnesium compounds to vegetation—a subject that was afterwards much discussed by TENNANT, DAVY, KNOP and other writers, even down to the present time.

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Joseph Priestley (1733-1804):— The errors of STAHL's phlogistic system are in no place made more apparent than in the works of JOSEPH PRIESTLEY, one of the leading figures in the history of chemistry and indeed one of the greatest in the history of mankind. He was a most versatile character and a prodigious worker. Judged by the titles of his 150 books and pamphlets, PRIESTLEY's interests were devoted about 50 percent to theology, 20 percent to chemistry, and the remaining 30 percent to politics, education, philosophy, history, economics, and general science. Chemistry with PRIESTLEY was only a major avocation and yet it is for his work in chemistry that he is now chiefly remembered.

He was born of lowly parentage near Leeds, England, and obtained his early education partly in neighboring schools and partly from self-instruction. At the age of 19 he entered Daventry Academy where he spent three years studying for the ministry. After serving several years as minister and teacher, PRIESTLEY accepted a tutorship at Warrington Academy where he first acquired a taste for natural science. During a visit to London in 1766 he met BENJAMIN FRANKLIN, a commissioner of the American Colonies, who became a life-long friend and stimulated his love for science and his liberal views in politics and religion. With FRANKLIN's help PRIESTLEY wrote his first scientific book, "The History and Present State of Electricity" which won wide recognition and secured his election to the Royal Society. In 1767 he accepted the pastorate of a church in Leeds and it was during this period that he made his first chemical experiments upon the "fixed air" of the fermenting vats in a brewery adjacent to his home. He was a self-made chemist and devised his own apparatus and processes. His method of impregnating water with fixed air (soda water) won him the Copley Medal of the Royal Society in 1773. In 1772 PRIESTLEY resigned his pastorate to become librarian and literary companion of Lord SHELBURNE, who with great generosity afforded him every opportunity for continuing his chemical experiments. This privilege was utilized to such advantage that the eight years of PRIESTLEY's connection with SHELBURNE were the most productive of his chemical career. On August 1, 1774, he first prepared oxygen, which in the language of the phlogistonists he called dephlogisticated air, and two months later, while visiting Paris with Lord SHELBURNE, he gave LAVOISIER an account of his discovery. He thus placed in the latter's hands the very instrument that was soon to demolish PRIESTLEY's cherished doctrine of phlogiston.

In 1780 PRIESTLEY left Lord SHELBURNE and accepted the pastorate of a Unitarian Church in Birmingham. His associations here with scientific and literary friends during the next ten years were the most pleasant of his life, but this happy period was only the calm that preceded the storm. PRIESTLEY's bold defense of the rights of the dissenting churches and his outspoken sympathy with the revolt of the laboring classes against political oppression in France aroused the animosity of the extreme partisans of Church and State. Their instigations inflamed the passions of a riotous

mob, which wreaked its vengeance upon PRIESTLEY by burning his church, his home and his laboratory. In his remonstrance to the citizens of Birmingham for this outrage PRIESTLEY declared:—

"You have destroyed the most truly valuable and useful apparatus of philosophical instruments that perhaps any individual in this or any other country was ever possessed of, in my use of which I annually spent large sums, with no pecuniary view whatever, but only in the advancement of science, for the benefit of my country and of mankind. You have destroyed a library corresponding to that apparatus which no money can repurchase, except in a course of time. But what I feel far more, you have destroyed *manuscripts*, which have been the result of the laborious study of many years, and which I shall never be able to recompose; and this has been done to one who never did, or imagined you, any harm" (THORPE 1906, pp. 135-6).

Because of the persistent ill will that had been aroused against him, even in scientific circles, PRIESTLEY decided to leave England and in 1794 emigrated to America where with the help of his sons he built a new home and laboratory at Northumberland, Pa. The house which he erected, remnants of his apparatus, and other personal relics are still preserved there as memorials. It was here in 1800 that he published his last, and what he regarded as his greatest, scientific work, "The Doctrine of Phlogiston established." It was the final argument written in defense of the long exploded hypothesis.

PRIESTLEY's chemical discoveries are contained in his famous "Experiments and Observations on different kinds of Air" first published in six volumes between 1774 and 1786. A later revised three-volume edition was published at Birmingham in 1790. It is from the latter edition that the citations, quoted in the present sketch, are taken.

In his preface to this work PRIESTLEY with characteristic candor admits the many mistaken conjectures which had crept into his writings as a result of his practice of immediate publication. He defends this policy, however, and is not ashamed of his wrong inferences, "being willing to encourage young adventurers, by shewing them that, notwithstanding the many errors to which even the most sagacious, and the most cautious, are incident, their labours may be crowned with considerable success." It is to this trait of freely confessing his own mistakes and of always acknowledging his indebtedness to other investigators that PRIESTLEY acquired a reputation for absolute fairness and integrity.

The agricultural chemist is chiefly interested in PRIESTLEY's experiments on plant and animal nutrition, and on putrefaction. His investigations covered a wide range of plant and animal substances—onions, carrots, parsnips, potatoes, turnips, peaches, lettuce, fish, meat, brains, blood, milk, urine, and bile.

PRIESTLEY's most important discovery was that of oxygen. It was made in the course of his experiments upon heating substances with a powerful burning glass in a closed glass vessel over mercury. His account of the episode is as follows:—

"On the 1st of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se* [mercuric oxide made by calcining mercury in the open air] and I presently found that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well

express, was, that a candle burned in this air with a remarkably vigorous flame" (*loc. cit.*, Vol. II, pp. 106-7).

PRIESTLEY also determined that a mouse could live three times longer in his new air than in common air. A more exact chemical comparison was obtained by PRIESTLEY's method of determining the contractions when measured volumes of the two airs were mixed with nitric oxide (PRIESTLEY's nitrous air).

"As common air takes about one half of its bulk of nitrous air, before it begins to receive any addition to its dimensions from more nitrous air, and this air took more than four half-measures before it ceased to be diminished by more nitrous air, and even five half-measures made no addition to its original dimensions, I concluded that it was between four and five times as good as common air" (*loc. cit.*, Vol. II, p. 119).

PRIESTLEY assumed that in this reaction phlogiston was given up by the nitric oxide and that the residue of unreactive gas (RUTHERFORD's mephitic air or nitrogen) was completely phlogisticated air. The new gas of superior reactive power, which was thought to contain no phlogiston, was therefore named dephlogisticated air. PRIESTLEY thus made the first chemical analysis of the atmosphere which he supposed to consist of one fourth to one fifth of dephlogisticated air and three fourths to four fifths of phlogisticated air.

The contraction which atmospheric air, or other gaseous mixtures, undergoes in the presence of an added volume of nitric oxide was PRIESTLEY's method of estimating its oxygen content. From his experiments date the beginning of eudiometric methods for determining the purity of air.

Theoretically two volumes of pure nitric oxide when mixed with one volume of pure oxygen should be completely absorbed by water as indicated by the equation $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. PRIESTLEY in his experiments owing to impurities in his gases or inaccuracies in his measurements, never obtained complete absorption. Usually the contraction of the 3 volumes of mixed gas was to half a volume which would indicate a purity for his oxygen of $2.5/3 \times 100$ or 83 percent. He reports having obtained contractions to one sixth of a volume equivalent to about 94 percent purity and in one case a contraction to three hundredths of a volume equivalent to 99 percent purity. In testing common air his practice was to use equal volumes of nitric oxide and air, in which case he reported usually a contraction from 2 volumes to 1.25-1.45 according to the purity of the air and conditions of the experiment. The theoretical value for atmospheric air of 21 percent oxygen by volume after mixing with an equal volume of NO is 1.37 volume. PRIESTLEY's eudiometric process for determining the oxygen content of the air with nitric oxide was a great advance, but it was subject to so many errors that it was soon superseded by more accurate methods.

PRIESTLEY employed the balance in many of his experiments but in marked contrast to LAVOISIER he failed to apply it rigidly in testing the correctness of his conclusions. He had a true picture of the arguments of LAVOISIER against the phlogistic doctrine but continued on the basis of his own observations to adhere to the view that metals were compounds of their calces and phlogiston. The following experiment, in which PRIESTLEY heated lead oxide with a burning lens in an atmosphere of hydrogen, is quoted as an illustration of his method of argument.

"I put upon a piece of a broken crucible (which could yield no air) a quantity of minium, out of which all air had been extracted; and placing it upon a convenient stand, introduced it into a large receiver, filled with inflammable air, confined by water. As soon as the minium was dry, by means of the heat thrown upon it, I observed that it became black, and then ran in the form of perfect lead, at the same time that the air diminished at a great rate, the water ascending within the receiver . . . seeing the metal to be actually revived, and that in a considerable quantity, at the same time that the air was diminished, I could not doubt, but that the calx was actually imbibing something from the air; and from its effects in making the calx into metal, it could be no other than that to which chemists had unanimously given the name of *phlogiston*" (*loc. cit.*, Vol. I, pp. 250-2).

If PRIESTLEY had performed this experiment over mercury and had carefully determined the weights of substances before and after the experiment he would have realized that the weight of metallic lead was less than that of the original minium and that the inflammable air had combined not with the minium to form lead but with the oxygen of the minium (a substance which he had used for liberating oxygen) to form water. In this as in all his other brilliant experimental work PRIESTLEY came close to the discovery of the truth that always elusively escaped from his grasp.

In a similar way PRIESTLEY assumed that the formation of water in the combustion of hydrogen, a discovery of CAVENDISH, was due to the fact that water "was an essential ingredient in the constitution of this kind of air". PRIESTLEY's explanation of the properties and composition of carbon monoxide which he prepared by heating "finery cinder" (black iron oxide) with charcoal is another example of false deduction. He reasoned that from its combustibility and from its leaving after ignition a residue that precipitated lime water the gas must be a compound of phlogiston and fixed air.

The nutritive principle in vegetable and animal substances according to PRIESTLEY was phlogiston. He remarks:—

"This principle is phlogiston, or the principle of inflammability, in such a state as to be capable of becoming, by putrefaction, a true inflammable air, but not generally such as to burn with explosions, but rather with a blue and lambent flame, mixed with a certain proportion of fixed air.

"In the putrefactive process the phlogiston is merely evolved, and not again combined with any thing, except what may be necessary to its assuming the form of inflammable air; but in nutrition it is immediately held in solution by the gastric juice, and in the chyle formed by it. But if any part of the aliment pass the stomach, and the first intestines, without having all its phlogiston incorporated with the chyle, that principle remains in the excrement, where it is often set loose in the form of inflammable air, the same form that it would have taken if it had gone through the simple putrefactive process. The phlogiston of the aliment, thus entering into the circulation with the chyle, after answering purposes in the animal oeconomy which are yet very imperfectly known to us, is thrown out again by means of the blood in the lungs, and communicated to the air, which is phlogisticated by it.

"All alimentary substances not only contain phlogiston, but I believe are capable of yielding a proper inflammable air by putrefaction" (*loc. cit.*, Vol. I, pp. 206-7).

PRIESTLEY believed that from a determination of the inflammable air produced in putrefaction

"it may be possible to determine the nutritive powers of different vegetable and animal substances, and also other problems in philosophy; though too much must not be expected from them.

"It might have been imagined, that by this means we should be able to ascertain the quantity of air that any mass of putrescent matter would thoroughly phlogisticate. For any given quantity of inflammable air will completely phlogisticate twice its bulk of common air" (*loc. cit.*, Vol. I, p. 217).

PRIESTLEY, however, failed to distinguish the difference in oxygen combining power (which he termed phlogistication) of the different inflammable airs produced in putrefaction. Thus 2 volumes of hydrogen would use up 1 volume of oxygen or 5 volumes of air, while 2 volumes of methane would use up 4 volumes of oxygen or 20 volumes of air.

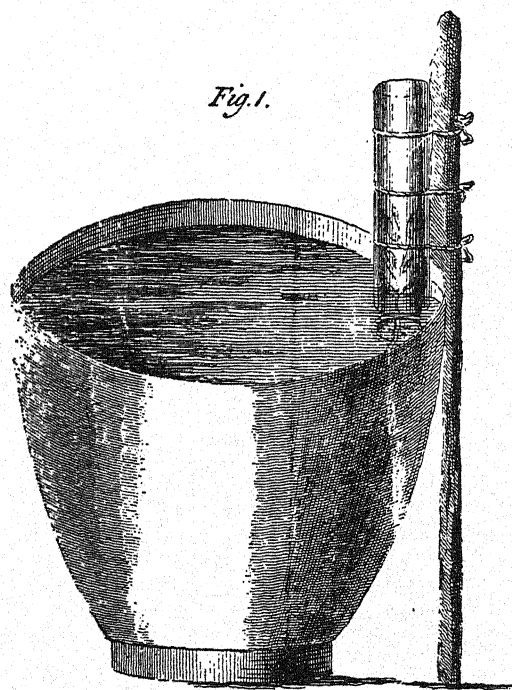


FIG. 21. — Priestley's apparatus for collecting the oxygen evolved by the leaves of green plants in water impregnated with fixed air and exposed to sun-light. — Plate VI in Vol. 3 of PRIESTLEY's "Experiments and Observations on different kinds of Air", Birmingham, 1790.

In trying to trace the rôle of phlogiston in plant and animal nutrition PRIESTLEY was chasing a will-o'-the-wisp and the value of this work is negative. Of vastly more importance to agricultural chemistry were his experiments upon the relations of plant and animal life to oxygen.

Even before the announcement of his discovery of oxygen PRIESTLEY had observed in August 1771 that a sprig of mint, when put into a closed volume of air in which a candle had burned out, would after ten days enable a candle to be burned in it again. Seven years later he repeated this experiment and ascertained that the purification of the air which he had observed in 1771 was due to the spontaneous emission from green plants of dephlogisticated air. PRIESTLEY's interesting account of this ob-

servation is so indicative of his method of experimenting that it is quoted herewith.

"Few persons, I believe, have met with so much unexpected good success as myself in the course of my philosophical pursuits. My narrative will show that the first hints, at least, of almost every thing that I have discovered of much importance, have occurred to me in this manner. In looking for one thing I have generally found another, and sometimes a thing of much more value than that which I was in quest of. But none of these unexpected discoveries appear to me to have been so extraordinary as that which I am about to relate; and it may serve to admonish all persons who are engaged in similar pursuits, not to overlook any circumstance relating to an experiment; but to keep their eyes open to every new appearance, and to give due attention to it, how inconsiderable soever it may seem.

"In the course of my experiments on the growth of plants in water impregnated with fixed air, I observed that bubbles of air seemed to issue spontaneously from the stalks and roots of several of those which grew in the unimpregnated water; and I imagined that this air had percolated through the plant. It immediately occurred to me, that if this was the case, the state of that air might possibly help to determine what I was at that time investigating, viz. whether the growth of plants contributes to purify, or to contaminate the air. For if this air should prove to be better than common air, I thought it would show, that the phlogiston of the imbibed air had been retained in the plant, and had contributed to the nourishment of it, while that part of the air which passed through the plant, having deposited its phlogiston, had been rendered purer by that means though if the air should not have been found better than common air, I should not have concluded my hypothesis was false; since plants, like animals, might take in phlogiston in one state, and emit it in another.

"With this view, however, I plunged many phials, containing sprigs of mint in water, laying them in such a manner, as that any air which might be discharged from the roots would be retained in the phials, the bottoms being a little elevated. In this position the sprigs of mint grew very well, and in some of the phials I observed a quantity of air to be collected, though very slowly; but I was much disappointed in finding that some of the most vigorous plants produced no air at all. At length, however, from about ten plants, I collected, in the course of a week, about half an ounce measure of air. This was the 19th of June, 1778; and, examining it with the greatest care, I found it so pure, that one measure of it and one of nitrous air occupied the space of only one measure" (*loc. cit.*, Vol. III, pp. 282-4).

PRIESTLEY's sample of air according to his eudiometric results was thus one half oxygen.

PRIESTLEY's supposition, that the absorption of the phlogiston of fixed air (carbon dioxide) by plants might be the controlling factor in the purification of air by vegetation, is a good illustration of how this investigator was hampered in all his experimental work by adherence to a false theory. He was even led to suppose that the phlogiston thus absorbed might be a source of food for plants for he had observed that mint growing in dephlogisticated air produced shoots of only about half the size of those grown in ordinary air. In this connection he remarks:—

"I do not say that even these observations are quite sufficient to determine the question; but they seem to make it probable, that dephlogisticated air does not supply that pabulum which plants derive even from common air; though I own it may injure them on some other account" (*loc. cit.*, Vol. III, p. 278).

Conferva, a green alga which thrives luxuriantly in stagnant water, proved to be a more satisfactory plant than mint for PRIESTLEY's experiments and his investigations with this vegetating organism have a particular interest. Water impregnated with carbon dioxide gave abundant growth of *Conferva* which was not the case with unimpregnated water (*loc. cit.*,

Vol. III, p. 287) and the gas evolved was rich in oxygen but free of carbon dioxide (*loc. cit.*, Vol. III, p. 311). PRIESTLEY observed also that sunlight seemed to be very necessary for the growth of *Conferva* for in darkness there was no development of the alga and no evolution of oxygen (*loc. cit.*, Vol. III, p. 290). It will be seen that PRIESTLEY had before him all the facts necessary for explaining the mechanism of the photosynthetic process of plants; he failed, however, to make this apparently obvious deduction.

In experiments, which PRIESTLEY conducted upon the behaviour of young willow plants in closed atmospheres of common air, he observed in some cases that from one half to seven eighths of the volume of air was absorbed. This experiment, apparently indicative of the absorption of atmospheric nitrogen, and other tests, in which hydrogen and nitric oxide also appeared to be absorbed, were probably vitiated by some unknown error of technique (*loc. cit.*, Vol. III, pp. 331-5).

The works of few great chemists afford the student so much enjoyment and instruction as those of PRIESTLEY. In no other writer can the reader follow so easily the steps by which great discoveries are made and at the same time glimpse so clearly the unexplored fields to which these discoveries open the way. For this reason PRIESTLEY's works were an inspiration to all his contemporaries and especially to LAVOISIER, who remarked that although his writings consisted "of a web of experiments almost uninterrupted by any reasoning" yet no other piece of recent work made him "appreciate more strongly how many new paths in physics and chemistry still remain to be trodden."

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Jan Ingen-Housz (1730-99):—INGEN-HOUSZ was a Dutch physician who having ample private means was able to devote much attention to scientific research. After practising medicine for six years in the Netherlands he transferred his residence in 1765 to London where he gained so much prestige among the scientists of that city that he was made a Fellow of the Royal Society. His skill in the treatment of smallpox by vaccination led to his being called to Vienna in 1768 as court physician to the royal family of Austria, several of whose members had fallen victims of a severe epidemic of this disease. After 10 years of successful practice in Vienna, during which other cities of Europe were visited, INGEN-HOUSZ resumed his residence in England. He went back in 1780 to Vienna, but the disturbed political conditions of Europe caused him in 1788 to return again to London where he spent the remaining 11 years of his life.

Stimulated by PRIESTLEY's investigations upon the rôle of plants in purifying the atmosphere, INGEN-HOUSZ began a similar series of experi-

ments. He noted the same as PRIESTLEY that green vegetation gives off oxygen in the presence of sunlight, but he made the additional important discovery that plants exhale carbon dioxide. During his second period in London INGEN-HOUSZ (1779) published the results of these investigations in his "Experiments upon Vegetables discovering their great Power of purifying the Common Air in the Sunshine and of injuring it in the Shade and at Night". The following summary is given by INGEN-HOUSZ in his introduction to this work:—

"I observed that plants not only have a faculty to correct bad air in six or ten days, by growing in it, as the experiments of Dr. PRIESTLEY indicate, but that they perform this important office in a compleat manner in a few hours; that this wonderful operation is by no means owing to the vegetation of the plant but to the influence of the light of the sun upon the plant. I found that plants have, moreover, a most surprising faculty of elaborating the air which they contain, and undoubtedly absorb continually from the common atmosphere, into real and fine dephlogisticated air; that they pour down continually, if I may so express myself, a shower of this depurated air, which, diffusing itself through the common mass of the atmosphere, contributes to render it more fit for animal life; that this operation is far from being carried on constantly, but begins only after the sun has for some time made his appearance above the horizon, and has, by his influence, prepared the plants to begin anew their beneficial operation upon the air, and thus upon the animal creation, which was stopt during the darkness of the night; that this operation of the plants is more or less brisk in proportion to the clearness of the day, and the exposition of the plants more or less adapted to receive the direct influence of that great luminary; that plants shaded by high buildings, or growing under a dark shade of other plants, do not perform this office, but, on the contrary, throw out an air hurtful to animals and even contaminate the air which surrounds them; that this operation of plants diminishes towards the close of the day, and ceases entirely at sunset, except in a few plants, which continue this duty somewhat longer than others; that this office is not performed by the whole plant, but only by the leaves and the green stalks that support them; that acrid, ill-scented and even the most poisonous plants perform this office in common with the mildest and the most salutary; that the most part of leaves pour out the greatest quantity of this dephlogisticated air from their under surface, principally those of lofty trees; that young leaves, not yet come to their full perfection, yield dephlogisticated air less in quantity and of an inferior quality, than what is produced by full-grown and old leaves; that some plants elaborate dephlogisticated air better than others; that some of the aquatic plants seem to excel in this operation; that all plants contaminate the surrounding air by night, and even in the day time in shaded places; that, however, some of those which are inferior to none in yielding beneficial air in sunshine, surpass others in the power of infecting the circumambient air in the dark, even to such a degree that in a few hours they render a great body of good air so noxious, that an animal placed in it loses its life in a few seconds; that all flowers render the surrounding air highly noxious, equally by night and by day; that the roots removed from the ground do the same, some few, however, excepted; but that in general fruits have the same deleterious quality at all times, though principally in the dark, and many to such an astonishing degree, that even some of those fruits which are the most delicious, as, for instance, peaches, contaminate so much the common air as would endanger us to lose our lives, if we were shut up in a room in which a great deal of such fruits are stored up; that the sun by itself has no power to mend air without the concurrence of plants, but on the contrary is apt to contaminate it" (*loc. cit.*, Introduction xxxiii-xxxviii).

INGEN-HOUSZ, like PRIESTLEY, failed to see the true import of his own experiments. He supposed that water, or some substance in the water, was changed into the vegetable substance of the alga which then, under the influence of sunlight, was in turn transformed into oxygen.

"This real transmutation," remarked INGEN-HOUSZ, "though wonderful in the eye of a philosopher, yet is no more extraordinary than the change of grass and other

vegetables into fat in the body of a graminivorous animal, and the production of oil from the watery juice of an olive tree."

As the historian of science reviews the conflict of chemical theories in the seventeenth and eighteenth centuries he is impressed with a certain similarity to the strife between the doctrines of the early Greek philosophers who attributed the manifold developments of the material world to transformations of one single primordial element which they variously believed to be earth, water, air or fire, as the case might be. VAN HELMONT believed as THALES that the bodies of plants and animals were transformation products of water and the French chemist BRACONNOT continued to preach this doctrine as late as 1806. TULL and DUHAMEL focussed their attention upon earth as the ultimate source of plant and animal food. STAHL and his followers, like HERACLITUS 22 centuries before, made fire the basis of their philosophic speculations. INGEN-HOUSZ and other chemists of the pneumatic school, following ANAXIMENES of the sixth century B. C., considered air to be the ultimate source of plant and animal food. The ease with which capable scientists can be misled in their speculations is nowhere more evident than in INGEN-HOUSZ's (1796) interesting "Essay on the Food of Plants and the Renovation of Soils", a work which because of its rarity seems to have been generally overlooked by agricultural scientists. In the beginning of this essay INGEN-HOUSZ suggested the following basic rule of agricultural chemical research:—

"The surest way to find out the real nourishment of organized bodies seems to be, to inquire what is the substance without which they inevitably perish and which alone is sufficient to continue their life" (*loc. cit.*, p. 1).

The erroneous assumption that only one substance is "the real nourishment of organized bodies" led INGEN-HOUSZ as it did other followers of this principle into a quagmire of false conclusions, among the chief of which was the old alchemistic doctrine of elementary transmutations.

"Now as . . . it seems to be probable," continues INGEN-HOUSZ, "that neither water nor soil is, or contains all the true nourishment of vegetables it must be concluded that plants must find it in the atmospheric air; for this is the only ingredient without which all vegetables perish. A plant shut up in vacuo soon dies; and it dies in all sorts of aerial fluids which are incapable of supporting animal life—such as fixed air, inflammable air, phlogisticated air, or azote, etc. It is true, Dr. PRIESTLEY and Mr. SCHEELE have propagated a doctrine diametrically opposite to what I have here advanced, by saying that plants thrive wonderfully in putrid air, and perish in pure air or dephlogisticated air. This doctrine, though generally adopted and very ingeniously applied, by Sir JOHN PRINGLE and others, to illustrate the mutual reference, established by the Author of Nature, between the vegetable kingdom and the animal creation, is refuted by my experiments, by which I think I have proved, that plants shut up in vital air live so much longer, as this air is superior in purity to atmospheric air. I have explained the manner of making these experiments with success and I have indicated the reason why, of two plants, the one shut up with common air, the other with the same quantity of vital air (both kept in the dark) the plant placed in common air can only be kept alive during a certain very limited time, whereas the plant shut up in vital air may be kept alive much longer, even as long as there is vital air enough remaining to cover the whole plant.

"From these and many other considerations, I have deduced, that from the two organized kingdoms, the animal and the vegetable, the animal derives its nourishment from the vegetable, but that the vegetable creation is independent of the animal world, provides for itself, and derives its subsistence chiefly from the atmosphere" (*loc. cit.*, p. 2).

In order to explain the false observation that plants can develop perfectly in pure vital air or oxygen INGEN-HOUSZ adopted the strange concept that plants have the faculty of transmuting the oxygen of the air into carbonic acid.

"The first operation of the embryo or beginning plant, is to decompose the air in contact with it, by changing the oxygenous part of it into carbonic acid, of which it probably absorbs, in the dark and shade, the oxygen and in the sunshine the carbon, throwing out at that time the oxygen alone and keeping the carbon to itself as nourishment" (*loc. cit.*, pp. 5-6).

It will be seen from this that INGEN-HOUSZ, to whom some historians of science attribute the discovery of the photosynthetic activity of plants, had a very erroneous conception of this process. INGEN-HOUSZ's transmutation ideas led him into other false conclusions.

"Without such like changes taking place in our organs," he asks, "how could we account for the generation of the great quantity of phosphoric acid existing almost everywhere in our bodies (which acid has already got the name, by some eminent chemists, of animal acid) principally in our bones? Whereas we find no where the marine acid, though of all others we take in the greatest quantity of it. . . . It seems, therefore, as if all the acids, the marine, vegetable, carbonic, etc., were in our organs transformed, for the greatest part, into the animal or phosphoric acid. It seems at least probable, that, without supposing this change of acids to take place in our bodies, we could not account for the great abundance of phosphoric acid existing in our bodies; for though it really exists in some of our foods, yet the quantity of it is but small" (*loc. cit.*, p. 4).

The roots of plants, according to INGEN-HOUSZ, perform a function only very subsidiary to that of the leaves.

"The roots," he continues, "take in, of course, all salts, earth, metallic substances, etc., that can be dissolved in water, or in the saline matter to be found in almost all waters. This solvent is found to be for the most part fixed air. Though we find some of these salts with all their characteristic qualities in some plants growing in a soil impregnated with them . . . yet it is not less true that the most part of the ingredients imbibed by the roots as well as by the leaves, trunk and branches, undergo almost a total change in the organs of plants, even so far as to produce in one plant a wholesome food, and in another its next neighbor a true poison. But as I have proved before that the atmosphere alone can furnish to some plants all that is wanting for all their functions we ought not to look too anxiously among rubbish or dung for the true and natural food of vegetables . . ." (*loc. cit.*, p. 10).

Of the needs of crops for the mineral elements of the soil INGEN-HOUSZ seems to have had not the slightest conception. He attributed the exhaustion of soils by plants to a depletion of their oxygen supply and the benefit of fallowing to a renewal of this acidifying principle. This idea led INGEN-HOUSZ to make the striking suggestion that the addition of strong mineral acids to the soil might take the place of fallowing: —

"It seems to be more than probable that the soil laying fallow attracts from the incumbent air more of the acidifying principle than it does when covered with plants. . . . Would it not from all these considerations taken together appear probable, that the oxygenous principle may be in a moment imparted to an exhausted soil, by pouring upon it, a little before the sowing of fresh corn, one of the most concentrated acids, much diluted by water or divided among a heap of earth? I am of opinion that the first trials, if thought worth while to be made, should be made with concentrated muriatic or vitriolic acid, principally the latter, by mixing it with a sufficient quantity of water or of dry sand or earth, so that it may be thrown or scattered over the ground as corn is usually sown" (*loc. cit.*, p. 18).

In accordance with this idea INGEN-HOUSZ conducted several small scale experiments upon the acidification of soils with apparently favorable results.

INGEN-HOUSZ, originally a phlogistonist, was more progressive than PRIESTLEY in accepting some of the new chemical doctrines of LAVOISIER, although his writings retained much of the nomenclature of the older philosophy. As in the case of many other chemists of this transition period the conclusions of his experimental work were often vitiated by the influence of tenaciously held obsolete opinions.

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Jean Senebier (1742-1809):— It remained for a Swiss clergyman and scientist, JEAN SENEBIER, to unravel the main aspects of the problem of photosynthesis to the solution of which PRIESTLEY and INGEN-HOUSZ had supplied the clues. SENEBIER was born at Geneva and at an early age showed a fondness for literature, philosophy, and science. His career in many ways resembled that of PRIESTLEY. Both men studied theology and became ministers, both were librarians, both suffered the misfortunes of political unrest, both were voluminous writers on a large variety of subjects, and both made chemistry their favorite avocation.

After completing his theological studies SENEBIER was admitted to the ministry in 1765. He filled a pastorate for several years and was then offered in 1773 the post of librarian of Geneva, a position which he occupied until his death except for a period of exile in the troubled years of the seventeen nineties. SENEBIER's library duties were not arduous and he had leisure for his studies in chemistry and plant physiology.

SENEBIER was a copious writer but his diffuse style, long sentences, repetitions and excessive attention to unimportant details tire even the most patient reader. He combined with the errors of the phlogiston doctrine, the fallacies of teleological reasoning. His speculations on final causes and the ways of Providence lead him often astray. The statement of INGEN-HOUSZ that plants pollute the air at night he regarded as a calumny of Nature and then declared:—

"NATURE will avenge herself by the facts that she has made me see and will prove always that her benefits to us will be found to increase in proportion as we investigate more deeply her wise and sublime processes" (SENEBIER 1782, Vol. I, p. 55).

In his plant physiological work SENEBIER tempered his praise of INGEN-HOUSZ with considerable criticism and a bitter controversy prevailed between these two investigators for a number of years upon questions of pri-

ority, correctness of results and other differences of opinion (SENEBIER 1788, Chap. I). This, the earliest of the numerous polemics, which have filled the pages of agricultural chemical literature, can still be read by the historical student with some degree of interest, but it was a trivial affair compared with the fierce controversies in the time of LIEBIG sixty years later. As usually happens in such disputes both men were partly in error. INGEN-HOUSZ overstated and SENEBIER understated the pollution of the air with carbon dioxide at night by living plants. SENEBIER, in the light of his later experiments, admitted with characteristic candor his early mistake upon this point.

The application of the new science of chemistry to the study of the phenomena of plant life was regarded in the beginning as an intrusion by some physiologists who looked upon chemistry as an upstart science that had no concern with the investigation of living matter. It was because of this prejudice that SENEBIER in the preface of his "*Recherches sur l'Influence de la Lumière Solaire*" devoted several pages to an apology for chemistry. This early defense of the new science of chemistry by SENEBIER has much historic interest and the following translation is given of several paragraphs from his "*apologie de la chymie*": —

"The new investigations, which I published in my *Mémoires Physico-chymiques*, printed in 1782, having a more chemical aspect than those which had previously appeared, I find myself obliged to make an apology for Chemistry, the applications of which to their operations some celebrated naturalists view with alarm, especially when it concerns the study of the vegetable kingdom. My respect for their opinion requires that I make known the grounds of my own views and their love for the truth leads me to hope that they will be glad to possess a new instrument for its discovery. . . .

"Why is Chemistry generally regarded as so strange among the sciences which relate to the investigation of natural phenomena? I know only one reason; it is because prejudice dominates the philosopher as much as it does him who is not a philosopher. When, however, we give the matter serious consideration we soon discover that Chemistry is nothing else than a branch of experimental Physics and one of its most useful branches. Could we at present hope for much progress in what are called Physics and Natural History without the aid of Chemistry? . . .

"It would seem then that if the knowledge of Physicists is still so restricted, it is because they have not employed Chemistry to widen their information. They do not know its resources because they do not know its methods. They regard the Chemist only as a common worker of metals or compounder of drugs without stopping to think that the true Chemist, who can qualify as a metallurgist and pharmacist, is above everything always a good Physicist—the only one capable of studying the operations of nature, of knowing the elementary constituents of bodies, of discovering the causes of their union, of unraveling the laws of their combinations and of understanding the effects which result therefrom" (SENEBIER 1783, pref. pp. iii, vi-vii, xii-xiii).

SENEBIER's great contribution to agricultural chemistry was his demonstration of the fact that the oxygen evolved by green plants was proportional to the amount of carbon dioxide present up to the point where an excess of the latter gas began to injure the vitality of the leaves. This is illustrated by the following experiments in which SENEBIER exposed to the sunlight the green leaves of different plants in vessels of recently boiled distilled water, variously charged with carbon dioxide. The volumes of oxygen evolved were measured in terms of the space occupied by grains of water (SENEBIER 1788, pp. 316-8).

AMOUNT OF SATURATION OF WATER WITH FIXED AIR	GRAINS OF WATER TO FILL SPACE OCCUPIED BY OXYGEN			
	1 leaf of peach tree	1 leaf of apricot tree	4 spears of grass	1 leaf of house- leek
Completely saturated	542	18	36	15
$\frac{3}{4}$ saturated water + $\frac{1}{4}$ boiled water..	398	274	406	2
$\frac{1}{2}$ saturated water + $\frac{1}{2}$ boiled water..	374	244	406	54
$\frac{1}{4}$ saturated water + $\frac{3}{4}$ boiled water..	70	166	142	42
Ordinary water	18 $\frac{1}{2}$	37	55	18 $\frac{1}{2}$
Boiled water	0	0	0	0

The experiments with several of the leaves indicate a suppression of the photochemical reaction with an excess of carbon dioxide. As a result of these and other experiments, SENEBIER concluded that the quantity of oxygen produced by green leaves in waters differently charged was proportionate to the amount of carbon dioxide present within the ranges which each leaf could tolerate.

SENEBIER found that plants by exhalation at night do not vitiate appreciably the open air of the fields where they are growing. No detectable differences were found by PRIESTLEY's nitric oxide test in the purity of the air by night or day. The case was different, however, with plants kept in a confined air space. Thus the air in a closed vessel over mercury, in which fresh leaves of peach trees were placed in darkness, showed the following contractions when measured samples were mixed with equal volumes of nitric oxide (SENEBIER 1788, p. 243).

Date:—	Volume after reaction (a)	Contraction 2—a
August 7.....	1.22	0.78
— 8.....	1.36	0.64
— 9.....	1.60	0.40
— 10.....	1.72	0.28
— 11.....	1.76	0.24
— 12.....	1.85	0.15
— 13.....	1.88	0.12

The estimated volume percentages of oxygen, according to the formula $\frac{100(2-a)}{3}$, indicate a diminution from 26 to 4, but because of the imperfections in the nitric oxide method the results are not exact and have only a comparative value. SENEBIER states that he was unable to obtain air more vitiated than the 1.88 test except when the leaves were allowed to ferment.

In order to determine the extent to which common air, vitiated in the above manner, could be restored by living green plants SENEBIER exposed raspberry leaves daily to the sunlight between 7 a.m. and 6 p.m. in an enclosed volume of the contaminated air and obtained the following contractions by the nitric oxide method. The experiment is the reverse of the one previously described (SENEBIER 1788, p. 242).

Date:—	Volume after reaction (a)	Contraction 2— a
Original contaminated air.....	1.47	0.53
August 7.....	1.10	0.90
— 8.....	1.09	0.91
— 9.....	1.06	0.94
— 10.....	1.03	0.97
— 11.....	0.99	1.01
— 12.....	0.96	1.06

The estimated volume percentages of oxygen, calculated as previously, show an apparent increase in this experiment from 18 to 35 which, as SENEBIER remarks, is greater than that of common air. If the contaminated air used in this experiment was produced by respiration alone, the restoration could not proceed farther than the 21 percent for common air. It is probable that the apparent excess of carbon dioxide in the contaminated air, beyond the respiration equivalent of 21 percent, was caused by a fermentation of the sugar in the leaves. SENEBIER in fact calls attention to the injury that leaves suffer when confined in this way (SENEBIER 1788, p. 233). He remarks that such experiments are not a perfect index of natural processes in the open air.

SENEBIER, like LAVOISIER, considered light to be an element (SENEBIER 1788, pref., p. ix), the union of which with the green leaf substance is the activating material that decomposes fixed air into dephlogisticated air (*i.e.*, carbon dioxide into oxygen). This union of light with leaf-substance was supposed to be prevented by the cold; hence the suspension of oxygen production at low temperatures. According to SENEBIER presence of fixed air, intensity of light, length of exposure, temperature, and state of leaf are the chief conditions that govern the photochemical production of oxygen by plants.

SENEBIER, like PRIESTLEY, was not convinced of the greater reasonableness of the new chemical system of LAVOISIER and remained a phlogistonist. In addition to his work upon photosynthesis he conducted miscellaneous investigations upon the spontaneous ignition of damp plant materials, the heat of plants, the improvement of eudiometers, and other chemical subjects.

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Henry Cavendish (1731-1810):— While the work of BLACK upon carbon dioxide did much toward destroying the ancient doctrine of an

elementary air, the final and decisive blows to this conception and to that of elementary water were given by the famous English chemist and physicist, HENRY CAVENDISH, who was the first to make determinations of the comparative weight and density of the different gases produced by the decomposition of plant and animal substances.

CAVENDISH obtained his primary education at Hackney School and then studied at Cambridge which he left, however, in 1753 without taking his degree. He was a man of very unsocial retiring disposition, whose sole interest in life seems to have been the acquisition of experimental knowledge for its own sake, with complete disregard of personal credit or priority of discovery. He lived a solitary life and, having inherited a large fortune, gave his entire attention to physical and chemical research. His first important contribution, "Three Papers, containing Experiments on factitious Air", was published in 1766 in the Philosophical Transactions of the Royal Society of which he became a fellow in 1760. The first of these papers deals principally with "Experiments on Inflammable Air", or hydrogen (THORPE 1921, pp. 78-87), which CAVENDISH prepared by the action of dilute sulfuric, or hydrochloric, acid upon metals. Like other phlogistonists he supposed the gas thus produced to come from the metal and to be a compound of phlogiston, if indeed it was not phlogiston itself. Although the production of inflammable air in this way had long been known there was no means of differentiating between the various kinds of inflammable air until CAVENDISH by carefully performed specific gravity determinations proved inflammable air, fixed air and other gases to be distinct entities. For the first time in the history of chemistry, laboratory experiments began to be conducted with careful attention to precise quantitative relationships. CAVENDISH found the density of hydrogen as compared with air to be 0.09 (actual 0.07) and that of carbon dioxide to be 1.57 (actual 1.53). While HALES and other investigators had made previous attempts to compare the weights of equal volumes of several so-called "airs", CAVENDISH was the first to prove that they have different densities.

CAVENDISH's third paper on "Factitious Air" reports "Experiments on the Air produced by Fermentation and Putrefaction" (THORPE 1921, pp. 96-101). He showed that the gas evolved in the alcoholic fermentation had the same specific gravity, solubility in water and action on flame as the fixed air from marble. The gas evolved in the putrefaction of "gravy-broth" was found to consist of a mixture of fixed air and inflammable air. The latter seemed to be "nearly of the same kind as that produced from metals" although certain slight differences led him to suspect that it might be contaminated with another heavier gas.

In January 1783 CAVENDISH (1783) read a paper before the Royal Society in which he described his new eudiometer for analyzing the air. During the eventful seventeen-year period since the presentation of his paper on "Factitious Air", revolutions had taken place in both the worlds of science and of politics. In 1772 RUTHERFORD under the direction of BLACK announced the presence in the atmosphere of mephitic air or nitrogen, in 1774 PRIESTLEY announced the discovery of another atmospheric constituent—dephlogisticated air or oxygen, while in 1777 LAVOISIER, by explaining the true nature of combustion, disproved the existence of phlo-

giston and inaugurated the movement which gave rise to modern chemistry.

PRIESTLEY, CAVENDISH, SCHEELE and other advocates of STAHL's phlogistic theory were slow, however, to give way and continued their allegiance to the doctrine which their own discoveries had been instrumental in overthrowing. They admitted the presence of two dissimilar gases in the atmosphere but explained their differences by assuming that the respirable, or flame-supporting, constituent was devoid of phlogiston (dephlogisticated) and that the mephitic or irrespirable constituent was saturated with it (phlogisticated). Combustion, decay, respiration, etc., by which oxygen is abstracted from the air were regarded as processes in which phlogiston was evolved and the atmospheric investigations of PRIESTLEY and of CAVENDISH were chiefly directed towards determining the amount of air which had not been contaminated by their hypothetical phlogiston.

The agent recommended by PRIESTLEY for absorbing the uncontaminated part of the air was nitrous air (nitric oxide) which was supposed to contain phlogiston. The union of the latter with the dephlogisticated air yielded a compound easily soluble in water and the shrinkage in volume of the reacting gases which PRIESTLEY had found in 1775 to be about one-fifth that of the air taken, was thus a measure of the purity (*i.e.*, oxygen content) of the air. CAVENDISH, in his eudiometric process of greater precision, employed the process of PRIESTLEY which he applied to many hundred analyses of air during a period of nearly sixty days in the latter part of the year 1781. As a general result of his experiments he came to the conclusion that the air is of uniform constant composition and "not sensibly more dephlogisticated on any one of the sixty days. . . . than the rest" (THORPE 1921, p. 140).

Pure dephlogisticated air or oxygen was found by CAVENDISH to have a contraction value on his eudiometer 4.8 times that of common air. From this value the oxygen content of the air is calculated to be $\frac{100}{4.8} = 20.83$ per cent which is very close to the present accepted value of 20.99 (THORPE 1921, pp. 21-2).

CAVENDISH (1784) made also a quantitative study of the phlogistication of air by means of burning hydrogen and during this work made the important discovery that water, which had been supposed for ages to be an elementary substance, was a compound of his dephlogisticated and inflammable airs. In this connection he made the following comment:—

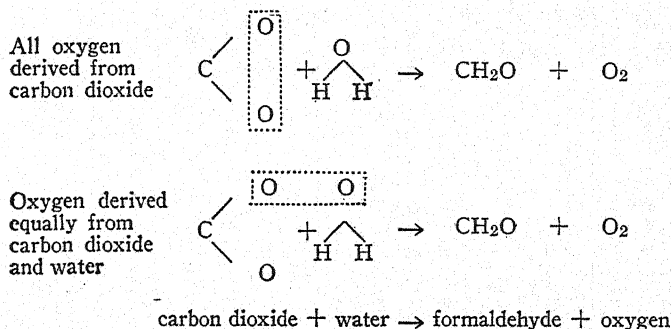
"It appears that 423 measures of inflammable air are nearly sufficient to completely phlogisticate 1000 of common air; and that the bulk of the air remaining after the explosion is then very little more than four-fifths of the common air employed; so that as common air cannot be reduced to a much less bulk than that by any method of phlogistication, we may safely conclude that when they are mixed in this proportion, and exploded, almost all the inflammable air, and about one-fifth part of the common air, lose their elasticity, and are condensed into the dew which lines the glass" (THORPE 1921, p. 166).

By collecting a considerable quantity of this so-called dew, CAVENDISH found it to consist entirely of water. The proportion of gases which reacted in its formation was approximately two volumes of hydrogen and one of oxygen.

The discovery of the compound nature of water caused CAVENDISH and other phlogistonists to adopt some strange readjustments of their views regarding the transmutations of their hypothetical element. The evolution of oxygen from the green leaves of plants when exposed to sunlight, as discovered by PRIESTLEY, was thus explained by Cavendish:—

“There is another way by which dephlogisticated air has been found to be produced in great quantities, namely the growth of vegetables exposed to the sun or daylight; the rationale of which in all probability is, that plants, when assisted by the light, deprive part of the water sucked up by their roots, of its phlogiston, and turn it into dephlogisticated air, while the phlogiston unites to, and forms part of, the substance of the plant” (THORPE 1921, p. 178).

In other words the hydrogen of the water is supposed to combine with the tissues of the plant and the oxygen to be liberated. Later experiments by SENEBIER seemed to indicate that the oxygen evolved by green plants is derived not from water but from carbon dioxide. The view of SENEBIER eventually prevailed but according to the modern view the oxygen evolved in the photosynthetic process is derived equally from water and carbon dioxide. The two types of reaction in modern notation can be represented hypothetically as follows:



In both types of reaction the end-products are the same and one volume of oxygen is evolved for each volume of carbon dioxide assimilated.

CAVENDISH, in continuing his interpretation of plant chemistry, further remarked:—

“Vegetables seem to consist almost entirely of fixed and phlogisticated air [*i.e.*, carbon dioxide and nitrogen], united to a large proportion of phlogiston [*i.e.*, hydrogen] and some water, since by burning in the open air, in which their phlogiston unites to the dephlogisticated part [*i.e.*, oxygen] of the atmosphere and forms water, they seem to be reduced almost entirely to water and those two kinds of air [carbon dioxide and nitrogen]. Now plants growing in water without earth, can receive nourishment only from the water and air, and must, therefore, in all probability, absorb the phlogiston from the water” (THORPE 1921, p. 179).

The newly expressed views of LAVOISIER regarding the evolution of oxygen from metallic oxides, nitrates and growing plants received favorable notice by CAVENDISH who preferred, however, to adhere to his old position. In this connection he remarked:—

“It seems, therefore, from what has been said, as if the phenomena of nature might be explained very well on this principle without the help of phlogiston; and, indeed, as adding dephlogisticated air to a body comes to the same thing as depriving it of its

phlogiston, and adding water to it, and as there are perhaps no bodies entirely destitute of water, and as I know no way by which phlogiston can be transferred from one body to another, without leaving it uncertain whether water is not at the same time transferred, it will be very difficult to determine by experiment which of these opinions is the truest; but as the commonly received principle of phlogiston explains all phenomena, at least as well as Mr. LAVOISIER's, I have adhered to that" (THORPE 1921, pp. 180-1).

In a paper presented before the Royal Society in June 1785 CAVENDISH (1785) describes his famous experiments "upon the conversion of phlogisticated air [*i.e.*, nitrogen] into nitrous acid" by means of the electric spark in presence of oxygen. By carefully regulating the proportion of the two gases he was able to remove by sparking all of the nitrogen of the air except a small residue which escaped conversion:—

"If there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than 1/120th part of the whole" (THORPE 1921, p. 193).

Without knowing it CAVENDISH by the isolation of this small residue of unconverted gas had prepared argon which was reisolated and identified by RAYLEIGH and RAMSAY in 1894.

The production of nitric acid by sparking in CAVENDISH's experiment is the first instance of the artificial fixation of atmospheric nitrogen, a process which over a century later was destined to become of such great importance to agriculture and industry. The explanation of this reaction according to the phlogiston doctrine led CAVENDISH to conclude that "phlogisticated air [nitrogen] is nothing else than nitrous acid united to phlogiston":—

"According to this conclusion," he remarked, "phlogisticated air ought to be reduced to nitrous acid by being deprived of its phlogiston. But as dephlogisticated air is only water deprived of phlogiston, it is plain, that adding dephlogisticated air to a body, is equivalent to depriving it of phlogiston, and adding water to it; and therefore, phlogisticated air ought also to be reduced to nitrous acid, by being made to unite to, or form a chemical combination with, dephlogisticated air; only the acid formed this way will be more dilute than if the phlogisticated air was simply deprived of phlogiston" (THORPE 1921, p. 191).

Although a man of great wealth CAVENDISH was wholly indifferent to its acquisition and display. He lived for his science alone with complete disregard of fame or publicity. In keeping with his solitary habits he died unattended on February 24, 1810 and was buried in All Souls' Church, Derby, with no tablet or memorial to mark his final resting place.

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Carl Wilhelm Scheele (1742–86):—The varied aspects of the phlogistic doctrine can be illustrated in no better way than by considering the work of C. W. SCHEELLE, whose brilliant investigations mark him as one of the greatest chemists of all time and whose early lamented death prevented him from realizing the true import of his own discoveries. He was born at Stralsund, then the capital of Swedish Pomerania, where he received his early education. Like many other famous chemists he began his career as a pharmacist and he continued as such until his death. During his apprenticeship at Gothenburg he gained familiarity with the works of NEUMANN, LEMERY, KUNCKEL, and particularly of STAHL, to whose phlogistic system of chemistry he became a most devoted adherent. In 1765 he moved to Malmö and then in 1768 to Stockholm where, as assistant to another apothecary, he made his first important discovery upon the isolation of tartaric acid from cream of tartar.

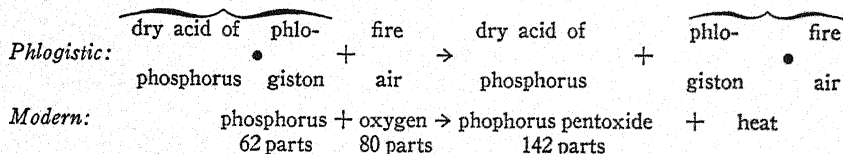
In 1770 SCHEELLE accepted another position with an apothecary in the university city of Uppsala where he lived for five years in most friendly relations with the great Swedish chemist BERGMAN. During this period he experimented on fluorspar and the compounds of manganese, isolated benzoic acid from gum benzoin, and discovered chlorine (which he named dephlogisticated marine acid air) and oxygen. Inspection of SCHEELLE's laboratory notes indicates that he had isolated oxygen as early as 1771, which was three years before its independent discovery by PRIESTLEY, who antedated SCHEELLE, however, by two years in the date of publication.

SCHEELLE's work on oxygen is contained in his only book, "*Chemische Abhandlung von der Luft und dem Feuer*," his famous "Chemical Treatise on Fire and Air" (DOBBIN, pp. 87–178), for which a preface was written by BERGMAN. Although published in 1777, the manuscript was given to the printer in 1775 and much of the experimental work was performed before 1773. In this work (sections 8–30) SCHEELLE proves air to consist of two "elastic fluids", one of which, making up about one third of the air, supports combustion (hence called by SCHEELLE "Fire-air", *i.e.*, oxygen); the other, constituting the remaining two thirds of the air, and "not in the least serviceable for the fiery combustion", he termed "Vitiated air" (*i.e.*, nitrogen). He removed oxygen from the air by employing liver of sulfur (potassium persulfide), burning phosphorus and other means and generated it by heating black oxide of manganese with sulfuric acid, by heating nitre, and in other ways. SCHEELLE's involved explanations of combustion, oxidation and other related phenomena illustrate, as in the cases of PRIESTLEY and CAVENDISH, the difficulties that beset the defenders of the phlogistic doctrine, as a result of the discovery of oxygen. Fire-air according to SCHEELLE was a compound of phlogiston and aerial acid (carbon dioxide). Heat and light, which SCHEELLE regarded as material substances, were supposed to be highly subtle, penetrating compounds of fire-air and phlogis-

ton. If the phlogiston was in still greater excess, "Inflammable Air" (*i.e.*, hydrogen) was thought to be produced. When substances were burned, or metals were calcined, phlogiston was supposed to be evolved and since phlogiston never existed uncombined it united with fire-air to produce heat which, escaping through the pores of the glass vessel, caused the contraction in volume which was such a puzzle to the old experimenters. This explanation resembles the one proposed by PHILO OF BYZANTIUM in the experiment of the burning candle. In this connection SCHEELE remarks: —

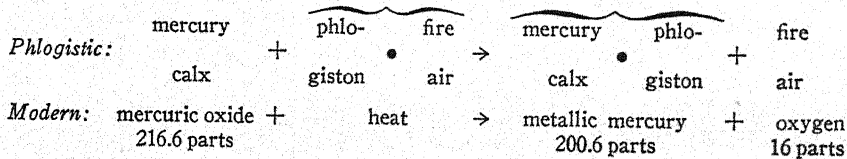
"I think I am not mistaken when I conclude from my experiments that the heat is really brought forth and produced in the first place from fire-air and the phlogiston of the inflammable substance; and if this newly generated, extremely subtle, elastic substance comes into contact with another which attracts phlogiston more strongly, then the heat must necessarily be again decomposed" (DOBBIN, p. 117).

A type of reaction in which SCHEELE supposed heat to be produced from fire-air and the phlogiston of an inflammable substance is that of burning phosphorus in an enclosed air space. The reaction in phlogistic and modern terms would be expressed as follows:



The escape of the supposed highly penetrative phlogiston · fire-air compound (*i.e.*, heat) through the pores of the glass was SCHEELE's explanation for the contraction in volume resulting from this reaction. The fact that phosphorus could be regenerated by heating its dry acid with substances rich in phlogiston, as charcoal, was one of the chief arguments employed by the phlogistonists in defense of their theory.

The production of oxygen and metallic mercury by heating mercuric oxide is a type of reaction in which heat was supposed to give up its phlogiston and regenerate the metal from its calx, while the other component of the heat (fire-air or oxygen) is liberated in the gaseous condition. The reaction in phlogistic and modern terms can be expressed as follows: —



The final results are the same with either type of reaction, but the difficulty with the phlogistic explanation is that the dry acid of phosphorus and calx of mercury lose instead of gain in weight after the supposed addition of phlogiston. This loss of weight, which could not be explained by the phlogistonists, was the crushing argument employed by LAVOISIER in the overthrow of their doctrine. SCHEELE admitted that "phlogiston is a material substance which always presupposes some weight" (Dobbin,

p. 102) and hence if the phlogistic explanation were correct, the weight of phosphorus and mercury should be greater and not less than that of the respective dry acid and calx.

SCHEELE describes many respiration experiments with plants, insects and other animals which he attempts to explain upon the basis of his phlogistic conceptions. The clumsy bladders which he employed for handling gases did not lead, however, to the accuracy that was obtained by CAVENDISH and LAVOISIER with their more highly perfected apparatus. SCHEELE's inability to obtain strong tests for carbon dioxide in his animal respiration experiments indicates faulty observation or technique while the strong production of carbon dioxide in his work with plants would seem to show that these experiments were conducted in the dark. His conception of the rôle of fire-air in plant metabolism was that the plant absorbed the phlogiston of the fire-air and liberated its carbon dioxide. He even supposed that the phlogiston of light and heat was similarly assimilated by plants for the elaboration of their combustible components. His statement "it is probable that all acids derive their origin from fire-air" is an anticipation of a similar view which was later expressed by LAVOISIER.

In a later publication on "Air and Fire and on the Generation of Water" (Dobbin, pp. 283-95) of the year 1785, when the phlogiston theory had been largely demolished by the work of LAVOISIER, SCHEELE made an unsuccessful effort to revise his theories of combustion in the light of the newer discoveries. He frankly admitted that prepossessed by older conceptions it never occurred to him to make weighings; and then he confessed: —

"There rise around me so many doubts that, before I am aware of it, I arrive in a labyrinth out of which I am scarcely in a position to find my way" (DOBBIN, p. 285).

He then made a final pathetic attempt to save his doctrine by modifying his earlier expressed views as to the nature of the fire-air which he had been the first to discover.

"I therefore regard fire air as an elastic fluid, consisting of a common, non-elastic, fundamental or saline principle; of a certain, although only a small quantity of phlogiston; and of a certain quantity of water" (DOBBIN, p. 286).

His applications of this revised opinion to the explanation of combustion and calcination led him, however, into conclusions that were fully as contradictory as those expressed in his earlier treatise.

But however great SCHEELE's failures may have been in defending STAHL's theory of phlogiston, they detract not in the slightest from the wealth and brilliance of his contributions to mineral, plant, and animal chemistry. In 1775 SCHEELE acquired the management of a pharmacy at Köping and here during the remaining eleven years of his short life he made many of his most important discoveries.

SCHEELE's investigations on arsenic acid in 1775 led him to the discovery of arsine and "SCHEELE's Green" (copper arsenite). The following year during his study of urinary calculi he isolated uric acid. He discovered hydrogen sulfide in 1777 and in the year following molybdic acid. In 1780 he isolated lactic acid from sour whey and studied its salts and chemical properties (DOBBIN, pp. 215-20); in this year also he prepared

mucic acid (which he called acid of sugar of milk) by oxidation of lactose with nitric acid. He prepared tungstic acid in 1781 from the mineral which in his honor was afterwards named scheelite (calcium tungstate). In 1782 SCHEELE made his celebrated experiments on the coloring matter of Prussian Blue, in the course of which he discovered prussic acid. He noted that the salt, extracted from the fusion of blood with potash (the so-called *lixivium sanguinis*), yielded, on distilling its solution with a little sulfuric acid, a volatile acid, which from its occurrence in Prussian Blue, was later termed prussic acid. In a remarkable series of ingenious experiments SCHEELE ascertained the chemical properties of this acid and described its odor and what is more remarkable its taste (BEDDOES 1901, p. 244). He was completely ignorant of the acid's toxicity and how he escaped from being poisoned has been something of a mystery.

Also in 1782 SCHEELE published a short chemical paper of practical agricultural interest of which the following translation is given: —

"Observations on a Method of Preserving Vinegar"

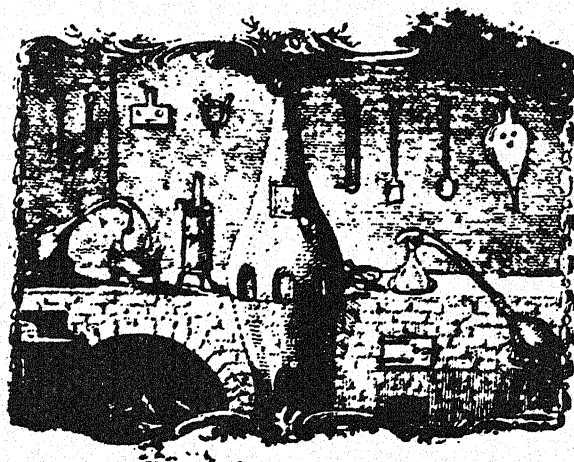
"It is a generally known fact that vinegar, of whatever kind it may be, cannot be preserved long, but after the lapse of a few weeks, especially in air at summer heat, becomes turbid and is covered upon the surface with a thick slime, whereby the acid is lost more and more and at last disappears entirely; for which reason it is often found necessary to throw away such vinegar. In order to prevent the corruption of the vinegar, four expedients have been discovered. The first is to brew a very strong and sour vinegar; it is known that such vinegar keeps for several years. But as there are not many who brew vinegar themselves, but content themselves with that which is commonly made for sale, there are only few who can make use of this method. The second is to strengthen the vinegar by means of freezing, when, be it noted, a hole is made in the ice crust and what does not freeze is filled into jars. This device is quite good, but as at least the half is lost by it, although that which forms the ice crust is nothing else than mostly water, our housekeepers will not like it. The third method is to exclude air from the vinegar, that is to keep the jars or bottles of it well filled and corked. Although the vinegar keeps for quite a long time by such a plan, still the method is not in use, probably because it may be difficult, as soon as some is used out of a bottle, to fill the latter again immediately with other clear vinegar from another bottle, whereby the vinegar in the bottle which then does not remain full and into which air consequently gets admitted, soon becomes turbid and spoils. To distil the vinegar is the fourth method for its preservation; such vinegar does not undergo the smallest change for many years in the air or in heat, but as it is more costly than undistilled, this method is not likely to come into use, especially as the following method of preserving vinegar is the easiest of all: Nothing more is required than to pour the vinegar into a well tinned kettle and to make it boil for a quarter of a minute over a strong fire and afterwards to fill it carefully into jars; or also, if it is believed that the tin is injurious to health, the vinegar can be poured into one or several bottles which are afterwards placed in a pot with water over the fire; after the water has boiled for a short time, the bottles are taken out of the pot. This vinegar thus boiled keeps many years free from slime and foulness, as well in the open air as in bottles half full; it is also quite suitable to use in apothecaries' shops, in place of the ordinary vinegar, for the compounded vinegars, which otherwise, in so far as distilled vinegar is not used soon enough, become turbid and at last lose the acid entirely" (DOBBIN, pp. 237-8).

SCHEELE's method of preserving vinegar by the action of heat is one of sterilization and is an anticipation of the process of food preservation announced by APPERT over twenty years later.

In 1783 SCHEELE isolated glycerol, which is considered by some to be his most important discovery next to those of chlorine and oxygen. His process is described in CRELL's *Chemische Annalen* (second part, p. 99)

under the title of "Discovery of a Peculiar Sweet and Volatile Matter, which is a Constituent Part of Expressed Oils and the Fat of Animals" (DOBBIN, pp. 255-8). His isolation of this sweet principle (*principium*

Carl Wilhelm Scheele's
p. Königl. Schwed. Acad. d. Wissenschaft. Mitgliedes,
Chemische Abhandlung
von der
Luft und dem Feuer.
Nebst einem Vorbericht
von
Torbern Bergman,
Chem. und Pharm. Prof. und Ritter; verschied.
Societ. Mitglied.



Upsala und Leipzig,
Verlegt von Magn. Swederns, Buchhändler;
zu finden bey S. L. Crusius.
1777.

FIG. 22. — Title page of SCHEELÉ'S "Chemische Abhandlung von der Luft und dem Feuer". First Edition, 1777. — Courtesy of the Amer. Phil. Soc.

dulce) was accomplished by boiling the oil or fat with water and litharge and then pouring off the water from which the glycerol was obtained by evaporation.

In his last years SCHEELE returned to his first work of 1768 on the vegetable acids. His "Observations on Lemon Juice and on the Method of Crystallizing It" (DOBBIN, pp. 259-62), published in 1784, describes the isolation of citric acid, and his article "On the Constituents of Earth of Rhubarb; together with the Method to Prepare the Acid of Sorrel" (DOBBIN, pp. 262-7), gives an account of his isolation and studies of oxalic acid.

Another article of SCHEELE in 1785 "On the Acid of Fruits and Berries" (DOBBIN, pp. 267-75) describes his isolation of citric acid from gooseberries and of malic acid from apples. In this article also he gives results of his tests for citric, malic, and tartaric acids in twenty common fruits and berries. A subsequent contribution of this same year "On the Presence of Earth of Rhubarb in Various Vegetables" (DOBBIN, pp. 281-2) reports the presence of calcium oxalate in 23 of 72 different officinal roots and in 15 of 19 different officinal barks. The list was extended the following year to 24 more roots and 16 more barks. One of the last papers by SCHEELE, entitled "On the Essential Salt of Galls, or Gall-Nut Salt" (DOBBIN, pp. 306-8) relates to the isolation and reactions of gallic acid.

SCHEELE's general method of isolating the vegetable acids consisted in treating the hot plant juice or extract with a weighed amount of pulverized chalk, filtering off the mixture of lime compounds, washing with hot water to remove impurities and then decomposing the precipitate with an amount of sulfuric acid equivalent to the weight of chalk first taken. After cooling, the insoluble sulfate of lime was filtered off and the vegetable acids recovered from the filtrate by crystallization.

SCHEELE was a self-taught chemist and it is remarkable that his laboratory researches were performed in the midst of the labors and cares of his pharmacy business. He was a modest unassuming man of almost saintly character and so indifferent to fame that although one of the greatest chemists of all time he lived and died in comparative obscurity. There is a tradition that the King of Sweden was once congratulated by FREDERICK THE GREAT on having so distinguished a man as SCHEELE for a subject, and that upon reaching home he inquired as to who this person might be. He was told there were two persons by the name of SCHEELE, one an obscure apothecary and the other an army officer. The King, supposing that so great a soldier as FREDERICK THE GREAT must have had the army officer in mind, made the latter a general and knighted him with the title VON SCHEELE. There are several versions of this story, one of which is told by DUMAS (1837) in his "Leçons sur la Philosophie chimique".

The work of SCHEELE in isolating so many new chemical compounds from plant and animal substances may be said to mark the beginning of accurate analytical research in the field of agricultural chemistry. We can appreciate this better by considering the vague divisions of the proximate constituents of plants into unctuous oils, mucilagenous juices, gummy juices, saponaceous juices, resins, volatile spirits, etc., that were employed by WALLERIUS and other writers when SCHEELE first began his work. It was SCHEELE's great service to depart from these ambiguous classifications of plant constituents and to begin substituting therefor organic compounds of a definite chemical nature. Agricultural chemistry thus began to assume for the first time the character of a modern science.

Had SCHEELE been as attentive as PRIESTLEY to the prompt publication of his laboratory investigations, he would have secured undisputed priority for a number of discoveries that have been accredited to others. His reticence and indifference to personal renown prevented him from acquiring as much immediate celebrity as some of his less gifted but more assertive contemporaries. Some writers have supposed that had SCHEELE's life been spared he would have soon abandoned the doctrine of STAHL for the more rational system of LAVOISIER. It cannot be said, however, that SCHEELE's adherence to the phlogistic school was an insurmountable obstacle to his laboratory investigations. His wonderful chemical genius was able to triumph over any possible theoretical handicaps. With such names as those of MARGGRAF, PRIESTLEY, CAVENDISH, and SCHEELE to its credit the phlogistic system, however irrational, cannot be dismissed as unproductive of great accomplishments.

The quotations from the works of PRIESTLEY, CAVENDISH, and SCHEELE illustrate how brilliant chemists may make great discoveries, although working upon the basis of an entirely false philosophy. It remained for the chemical genius of LAVOISIER to disentangle the discoveries of the phlogistonists from the complicated trappings of their confused explanations and by laying the foundations of a new rational system to set chemistry upon the true road of progress and discovery.

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Chapter VI

AGRICULTURAL CHEMISTRY DURING THE CHEMICAL REVOLUTION

Antoine Laurent Lavoisier (1743-94): — The final overthrow of the doctrine of phlogiston and the establishment of the foundation of the structure of modern chemistry are due almost entirely to the work of the great French chemist ANTOINE L. LAVOISIER. Yet the work of LAVOISIER consisted more in giving a correct interpretation to facts already known, than in making new discoveries. As LIEBIG remarked in the third of his "Chemical Letters": —

"He discovered no new body, no new natural phenomenon; all the facts established by him were the necessary consequences of researches that had preceded his own. His immortal service consisted in endowing the body of the science with a new spirit; but all the members of that body were already present and correctly united."

LAVOISIER developed an early taste for natural science. His first chemical training was obtained under G. F. ROUELLE (1703-70) at the Jardin du Roi in Paris. In 1766 he received a gold medal from the Academy of Sciences for an essay on the best method of illuminating streets and from this time his advancement in the fields of theoretical and applied chemistry was rapid. He was appointed a member of the governmental Gunpowder Committee in 1775 and in this position greatly increased the production of saltpeter and improved the manufacture and quality of gunpowder. Among other governmental appointments held by LAVOISIER was that of secretary to the committee on agriculture in which capacity he issued reports on the cultivation of different crops and made suggestions for the establishment of agricultural experiment stations. He conducted an experimental farm at Fréchine where he gave demonstrations upon improved methods of farm management and rural economy. He was a commissary of the treasury and was interested in the improvement of the social, economic, and financial conditions of France. He was one of the farmers-general of the public revenue, whose unpopularity at the time of the Revolution led to the execution of many of its members. Among these was LAVOISIER himself who suffered death by the guillotine on May 8, 1794. As LAGRANGE remarked at the time: "They needed only a moment to take off his head and more than a hundred years perhaps will elapse before another one like it will be produced".

The first summation of LAVOISIER's new system of chemistry is contained in his "*Traité élémentaire de chimie présenté dans un ordre nouveau et d'après les découvertes modernes*" published in two volumes at Paris in 1789. Translations of this work in English, German, Italian, and Dutch brought a wide acceptance of the new views and before the end of the century but few supporters were left of the old phlogistic doctrine. The translation of ROBERT KERR of Edinburgh under the title, "*Elements of Chemistry in a new systematic order containing all the modern discoveries*", in its several editions in Edinburgh and in New York (1806), gave the work an extensive notice in English speaking countries. The complete

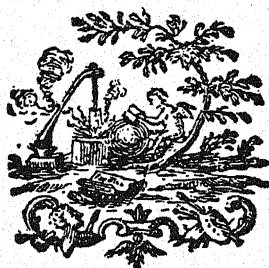
"Oeuvres de LAVOISIER" were published at Paris in six large volumes under the direction of the French Minister of Public Instruction between the years 1862 and 1893. It is to this work and to the third edition (1796) of KERR'S

TRAITE
ÉLÉMENTAIRE
DE CHIMIE,
PRÉSENTÉ DANS UN ORDRE NOUVEAU
ET D'APRÈS LES DÉCOUVERTES MODERNES;

Avec Figures :

Par M. LAVOISIER, de l'Académie des
Sciences, de la Société Royale de Médecine, des
Sociétés d'Agriculture de Paris & d'Orléans, de
la Société Royale de Londres, de l'Institut de
Bologne, de la Société Helvétique de Basle, de
celles de Philadelphie, Harlem, Manchester,
Padoue, &c.

TOME PREMIER.



A PARIS,
Chez CUCHET, Libraire, rue & hôtel Serpente.

M. DCC. LXXXIX.

Sous le Privilège de l'Académie des Sciences & de la
Société Royale de Médecine.

FIG. 23.— Title page of the first edition of LAVOISIER'S "Traité Élémentaire de Chimie", Paris, 1789.

English translation of the Traité Élémentaire that the following citations refer.

The fundamental basis of LAVOISIER'S new chemical philosophy is contained in the following statement: —

"We may lay it down as an incontestible axiom, that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity of the elements remain precisely the same; and nothing takes place beyond changes and modifications in the combinations of these elements. Upon this principle, the whole art of performing chemical experiments depends: We must always suppose an exact equality between the elements of the body examined, and those of the products of its analysis" (KERR, p. 187; Oeuvres, Vol. I, p. 101).

It was by means of numerous carefully conducted quantitative experiments with the balance that LAVOISIER arrived at the truth of this axiom. It was thus that in 1770 he disproved the old doctrine that water could be transmuted into earth by repeated distillations. He showed that the total weight of a sealed glass vessel of water remained constant, however long the water was boiled. At the end of the experiment the water was found to contain a weight of earthy matter in solution, which was exactly equal to the loss in weight of the flask. The inescapable conclusion, therefore, was that the earth was dissolved from the flask and was not a transmutation product of the water.

In the same way in 1772 he showed that when phosphorus and sulfur are burned in sealed vessels containing air there were no changes in the weights of the systems as a whole. The phosphorus and sulfur on combustion increased in weight by exactly the same amount which the air had lost. The inference again was that these substances had combined with a constituent of the air and not that they had given off phlogiston. When PRIESTLEY announced the discovery of "dephlogisticated air" in 1774, LAVOISIER identified this new gas as the atmospheric constituent that entered into combination in the process of combustion and since the combustion products of sulfur, phosphorus, and carbon were all of an acid nature LAVOISIER suggested in a memoir presented to the Academy in 1777 that "dephlogisticated air" be given the name oxygen (from the Greek *ὄξύς* acid and *γεννάω* I produce). The belief expressed by LAVOISIER that all acid substances must contain oxygen was not definitely disproved until many years later.

The irrespirable constituent of the atmosphere, the so-called "mephitic air" of RUTHERFORD, was renamed azote by LAVOISIER (from the Greek *α* privative and *ζωή* meaning life, *i.e.*, not supporting life), a term still employed in France, although not accepted in other countries. "Inflammable air" from its property of producing water when burned with oxygen was renamed hydrogen (from the Greek *ὑδωρ* water and *γεννάω* I produce). LAVOISIER's original table of chemical elements, the prototype of all subsequent tabulations of this kind, is reproduced herewith.

Although from the very beginning of his work LAVOISIER was aware of the fallacies of the phlogistic doctrine it was not until 1783 that he gave the final coup de grâce to this theory in his celebrated "Réflexions sur le phlogistique." This criticism exposes with unanswerable arguments the inconsistencies in which the followers of STAHL were obliged to take refuge in defense of their system. LAVOISIER remarks:—

"Chemists have made of phlogiston a vague principle which is not rigorously defined and which consequently can be adapted to explain everything for which it is required. Sometimes this principle is heavy, sometimes it is not; sometimes it is free

TABLEAU DES SUBSTANCES SIMPLES.

	Noms nouveaux.	Noms anciens correspondans.
<i>Substances simples qui appartiennent aux trois règnes & qu'on peut regarder comme des élémens des corps.</i>	Lumière.	Lumière.
	Calorique.	Chaleur.
		Principe de la chaleur.
		Fluide igné.
		Feu.
		Matière du feu & de la chaleur.
	Oxygène.	Air déphlogistiqué.
		Air empiréal.
		Air vital.
		Base de l'air vital.
<i>Substances simples non métalliques oxidables & acidifiables.</i>	Azote.	Gaz phlogistiqué.
		Mofète.
	Hydrogène.	Base de la mofète
		Gaz inflammable.
	Soufre.	Base du gaz inflammable.
		Soufre.
	Phosphore.	Phosphore.
	Carbone	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique.	Inconnu.
	Radical boracique.	Inconnu.
	Antimoine.	Antimoine.
	Argent.	Argent.
	Arsenic.	Arsenic.
	Bismuth.	Bismuth.
<i>Substances simples métalliques oxidables & acidifiables.</i>	Cobalt.	Cobalt.
	Cuivre.	Cuivre.
	Étain.	Étain.
	Fer.	Fer.
	Manganèse	Manganèse.
	Mercure.	Mercure.
	Molybdène.	Molybdène.
	Nickel.	Nickel.
	Or.	Or.
	Platine.	Platine.
	Plomb.	Plomb.
	Tungstène.	Tungstène.
	Zinc.	Zinc.
	Chaux.	Terre calcaire, chaux.
	Magnésie.	Magnésie, base du sel d'epsom.
<i>Substances simples salifiables terreuses.</i>	Baryte.	Barote, terre pesante.
	Alumine.	Argile, terre de l'alun, base de l'alun.
	Silice.	Terre siliceuse, terre vitrifiable.

OBSERVATIONS

FIG. 24. — Lavoisier's Table of the Elements. — Reproduced from the first edition of his "Traité Élémentaire de Chimie." — Courtesy of the Widener Library of Harvard University.

fire, sometimes it is fire combined with an earthy element; sometimes it passes through the pores of vessels, sometimes they are impenetrable to it; it explains at the same time causticity and non-causticity, transparency and opacity, color and the absence of color. It is a vertiable Proteus that changes its form every moment" (Oeuvres II, p. 640).

Although rejecting the applications which the phlogistonists made of their doctrine, LAVOISIER was a firm believer the same as STAHL in the existence of an elementary principle of fire.

"The partisans of the phlogistic doctrine," he remarked, "do not surpass me on this point and if the existence of an igneous fluid is an hypothesis, it is common to their system and to mine" (Oeuvres II, p. 641).

LAVOISIER thus admits to being a modified sort of phlogistonist and relics of STAHL's doctrine entered in fact into his own system of chemistry. Just as SCHEELE supposed his fire-air and inflammable air to be compounds of phlogiston so LAVOISIER could not divorce himself from this idea and regarded oxygen, hydrogen, and other gases not as elements but as compounds of these elements with the hypothetical imponderable caloric (Chap. I of *Traité élémentaire*). Substitute the word caloric for phlogiston and LAVOISIER would agree with the phlogistonists in explaining the liberation of heat, when a gas is compressed, or enters into combination, as due to the escape of a combined igneous element. Gaseous oxygen, according to LAVOISIER, had a stronger affinity for sulfur, phosphorus, carbon, metals, etc., than for caloric and in uniting with these substances its combined caloric was released as heat. LAVOISIER included the two imponderables light and heat in his table of elements and this practice was continued for nearly forty years after his death. The old tradition of the elementary nature of fire, held by the Greek philosophers and the phlogistonists, left its impress even upon LAVOISIER, who died in the belief of an imponderable *matière du feu*.

The experiments of LAVOISIER that chiefly interest the agricultural chemist are those relating to the basic phenomena of fermentation, animal respiration, and calorimetry. The following passage is quoted from LAVOISIER's description of his fermentation experiment: —

"I did not make use of the compound juices of fruits, the rigorous analysis of which is perhaps impossible, but made choice of sugar, which is easily analysed, and the nature of which I have already explained. This substance is a true vegetable oxyd with two bases, composed of hydrogen and carbon, brought to the state of an oxyd, by means of a certain proportion of oxygen; and these three elements are combined in such a way, that a very slight force is sufficient to destroy the equilibrium of their connection. By a long train of experiments, made in various ways, and often repeated, I ascertained that the proportion in which these ingredients exist in sugar, are nearly 8 parts of hydrogen, 64 parts of oxygen, and 28 parts of carbon, all by weight, forming 100 parts of sugar.

"Sugar must be mixed with about four times its weight of water, to render it susceptible of fermentation; and even then the equilibrium of its elements would remain undisturbed, without the assistance of some substance to give a commencement to the fermentation. This is accomplished by means of a little yeast from beer; and, when the fermentation is once excited, it continues of itself until completed" (KERR, *loc. cit.*, pp. 188-9; Oeuvres, Vol. I, pp. 101-2).

The balance of elementary composition in this experiment before and after fermentation was given by LAVOISIER (OEUVRÉS, Vol. I, pp. 102-6)

in terms of the old French system of weights in which 1 pound (0.93 English lb.) = 16 ounces; 1 ounce = 8 gros; 1 gros = 72 grains. The decimal weights, as calculated by KERR (*loc. cit.*, pp. 190-3), are quoted in the following tabulation:—

Materials of Fermentation:—

Water	lbs.
Sugar	400.
Yeast in paste {	
Water	7.2391493
Dry yeast	2.7608507
Total	510. lbs.

Elementary Composition of Materials of Fermentation:—

		lbs.
407.2391493 lbs. of water =	{	Hydrogen 61.0858724
		Oxygen 346.1532769
100 lbs. of sugar =	{	Hydrogen 8.
		Oxygen 64.
		Carbon 28.
2.7608507 lbs. of dry yeast =	{	Hydrogen .2900716
		Oxygen 1.6437457
		Carbon .7876519
		Azote .0393815
	Total	510. lbs.

Elementary Composition of Products of Fermentation:—

35.3458116 lbs. of carbonic acid =	{	Oxygen 25.4490017
		Carbon 9.8968099
408.9780816 lbs. of water =	{	Oxygen 347.6314019
		Hydrogen 61.3466797
57.7016059 lbs. of dry alcohol =	{	Oxygen combined with hydrogen 31.3897570
		Hydrogen combined with oxygen 5.5393880
		Hydrogen combined with carbon 4.0390625
		Carbon combined with hydrogen 16.7333984
2.500 lbs. of dry acetous acid =	{	Hydrogen1562500
		Oxygen 1.7187500
		Carbon6250000
4.0940755 lbs. of residual sugar =	{	Hydrogen3275825
		Oxygen 2.6201172
		Carbon 1.1463758
1.3804254 lbs. of dry yeast =	{	Hydrogen1450738
		Oxygen8218317
		Carbon3938802
		Azote0196397
510. lbs.		510. lbs.

The exact balance of elementary components in this first attempt to formulate the conversion of sugar into alcohol and carbon dioxide is only schematic, for as LAVOISIER himself remarked he had worked with only a few pounds of sugar and then calculated the results to a 100 lb. basis. The analyses were thus expressed to a degree of refinement impossible of attainment in actual work. Such an exact balancing of results, as indicated in the previous table, implies a certain amount of arithmetical "doctoring".

Although LAVOISIER had established the fundamental principles of combustion organic analysis, by which carbon is determined as carbon dioxide and hydrogen as water, his analyses of sugar, alcohol, and acetic acid are highly inaccurate because of the unfinished state to which he had developed the art. His determinations of carbon are much too low and those of oxygen too high, as is seen from the following tabulation:—

	<i>Actual percentages</i>			<i>Found by Lavoisier</i>		
	<i>Carbon</i>	<i>Hydrogen</i>	<i>Oxygen</i>	<i>Carbon</i>	<i>Hydrogen</i>	<i>Oxygen</i>
Sugar ($C_6H_{12}O_6$) ...	40.0	6.7	53.3	28.0	8.0	64.0
Alcohol (C_2H_6O) ...	52.2	13.0	34.8	29.0	16.6	54.4
Acetic acid ($C_2H_4O_2$)	40.0	6.7	53.3	25.0	6.3	68.7

His yield of alcohol from 96 lbs. of fermented sugar was 60.0 percent and that of carbonic acid was 36.8 percent. The alcohol was evidently highly contaminated with water and the yield of carbonic acid, as in his other analyses, was much too low.

Emphasis should not be laid, however, upon the artificiality and quantitative errors of this tabulation but upon LAVOISIER's announcement for the first time of the principle that the process of fermentation like other chemical reactions could be formulated as a balanced equation according to his axiom that

"in all the operations of art and nature nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity remain precisely the same; and nothing takes place beyond changes and modifications in the combinations of these elements."

Here, as in his other references, LAVOISIER indicated the true method of chemistry. All that remained for subsequent investigators was to perfect the methods of organic analysis according to the plan which he had originated and to insert more accurate analytical results in the outline which he had proposed.

Even more important and striking were LAVOISIER's experiments upon animal nutrition, for it was he who by exact scientific methods first established the identity of the processes of combustion and respiration—an identity dimly perceived by the old Roman wine makers who tested the respirability of the air in their fermenting vats by a burning candle, more clearly apprehended by MAYOW in his experiments upon the vitiation of air by a burning candle and a breathing animal, but completely befogged by the phlogistonists who, while recognizing a certain similarity in the processes of calcination, combustion, and respiration, assumed that in each case the air became impregnated with phlogiston. Phlogistication of the air was the explanation of its irrespirable nature after the unlike processes of calcination and respiration. That extinguishment of flame and asphyxiation might be due to two dissimilar causes thus escaped notice, although it had been clearly indicated in 1772 by RUTHERFORD who showed that when a small animal was allowed to breathe the air in a confined space and the carbon dioxide thereby produced was removed by absorption with alkali, a gas (mephitic air) still remained which was incapable of supporting respiration or combustion. LAVOISIER clearly recognized the differences in nature between mephitic air and fixed air and emphasized the absolute in-

ertness of the mephitic component (nitrogen) of the air in the process of respiration.

The first step in demonstrating the identity of the two processes of combustion and respiration was LAVOISIER's proof that the *gas sylvestre* of VAN HELMONT and the fixed air of BLACK was a compound of carbon and oxygen, to which, because of its acidic character, he gave the new name of carbonic acid. Since carbonic acid was a product of respiration, as well as of combustion, the next step in the argument was the natural inference that breathing was essentially a process of combustion in which the oxygen of the air united with the carbonaceous matter of the blood. It being assumed that a greater amount of caloric was combined with gaseous oxygen than with gaseous carbonic acid, then according to the reasoning of LAVOISIER, heat must be liberated in both combustion and respiration in proportion to the amount of oxygen consumed. Animal heat would thus be identical in nature with heat of combustion. If the measurement of the heat generated in the two processes bore the same relationship to the amount of oxygen consumed and the amount of carbonic acid evolved, then the identity of the chemical nature of combustion and respiration would be firmly established.

In the experimental demonstration of this concept LAVOISIER enjoyed the collaboration in 1779 and 1780 of the eminent mathematician LAPLACE. One of the first results of their joint endeavor was the invention of an improved form of ice-calorimeter. This apparatus consisted of a cylindrical vessel with three concentric circular compartments; the outer compartment was closely packed with snow to exclude outside radiation; the middle compartment contained a weighed amount of ice; the innermost central compartment was reserved for the production of heat by combustion or by a breathing animal. The amount of ice melted was a measure of the heat evolved, while determinations of the oxygen consumed and of the carbon dioxide evolved supplied the chemical data for correlating the results. A calorimeter of this construction can still be seen in the collection of LAVOISIER's apparatus in the Conservatoire des Arts et Métiers in Paris. It is historically important as being the first type of the modern respiration calorimeter.

The following pounds of ice were reported by LAVOISIER to have been melted by one pound each of carbon, hydrogen and wax (OEUVRES, Vol. I, pp. 81-4; KERR, *loc. cit.*, pp. 155-9).

1 lb. carbon on burning melted.....	96.50000 lbs. of ice
1 lb. hydrogen on burning melted.....	295.58950 lbs. of ice
1 lb. wax taper on burning melted.....	133.16670 lbs. of ice

LAVOISIER's analysis of the wax indicated 82.29 percent carbon and 17.72 percent hydrogen. The calculated amounts of ice melted for these percentages would then be

.8229 lbs. carbon.....	79.39390 lbs. ice melted
.1772 lbs. hydrogen.....	52.37605 lbs. ice melted

Total	131.76995 lbs. ice melted
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which agrees fairly well with the result found by experiment.

In the early experiments with guinea pigs LAVOISIER and LAPLACE obtained an amount of melted ice considerably higher than that calculated

from the normal yield of carbon dioxide eliminated by the animal. This discrepancy he attributed in part to several causes (1) the effect of cold in increasing the carbon dioxide of the animal, (2) lowering the temperature

Fig. 3.

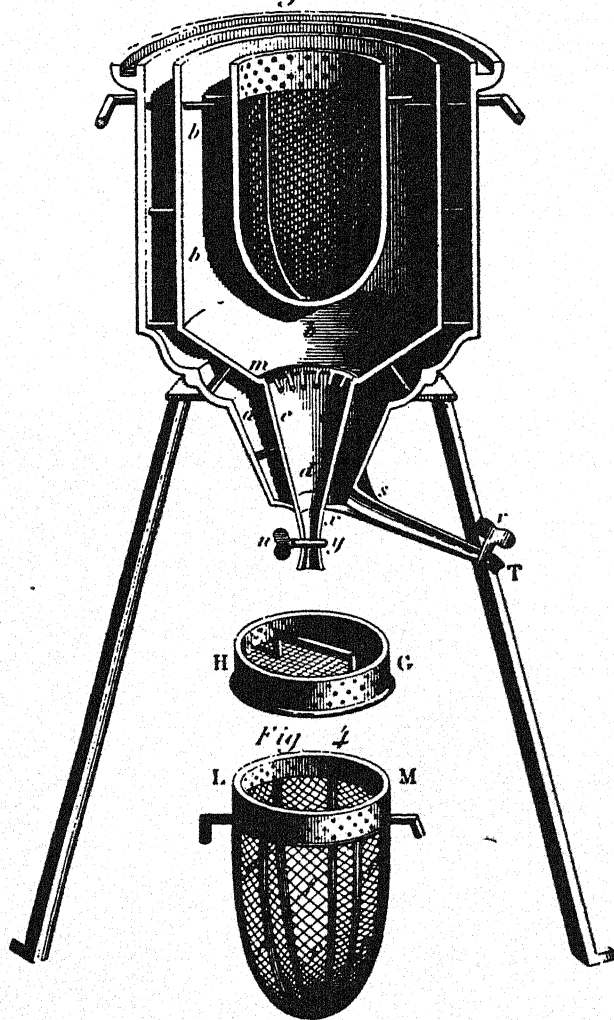


FIG. 25a. — *The Ice Calorimeter of Lavoisier and Laplace.* — The substance to be burned, or the experimental animal is placed in the inner wire basket ff (shown in detail with cover in Fig. 4). The middle circular space bb, outside the basket, is filled with crushed ice. The outer circular space aa is also filled with crushed ice to secure insulation. The water melted from the ice in bb by the heat of the burning substance, or animal, is drawn off at the bottom into the receptacle (Fig. 25b) and from its weight the liberated caloric, is calculated. — Illustration from LAVOISIER'S "Traité Élémentaire de Chimie".

of the animal and (3) condensation of respiration water. After the discovery of hydrogen and its oxidation to water by CAVENDISH in 1781 LAVOISIER came to realize that when oxygen is absorbed during respiration

a considerable part of it is used for the oxidation of hydrogen to water as well as for the oxidation of carbon to carbon dioxide and he thus explained the greater part of the discrepancy observed in his earlier experiments.

Fig. 1^{re}

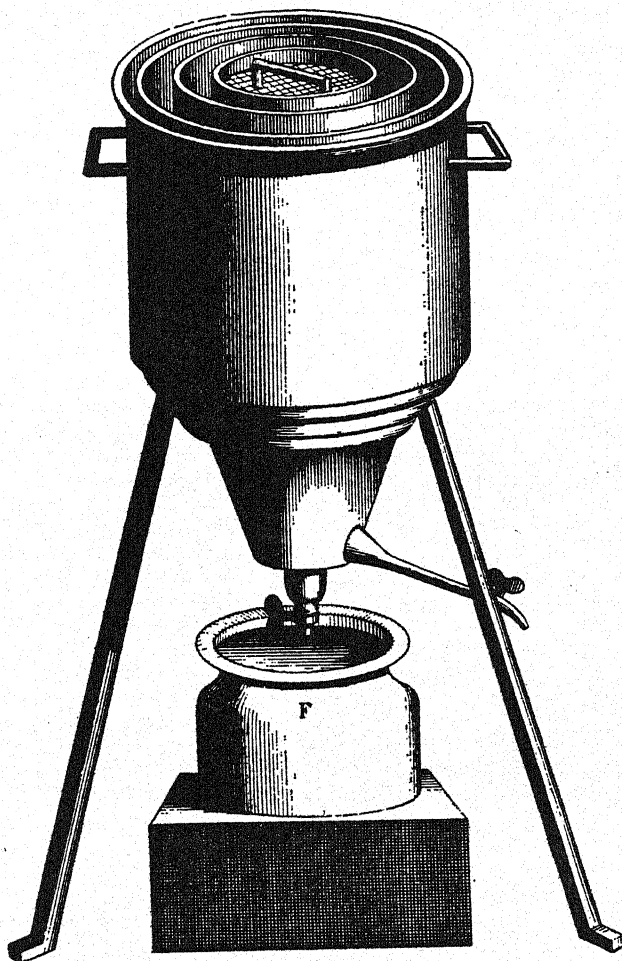


FIG. 25b. — For legend see previous page.

The following translations are of selections from the first Memoir of SEGUIN and LAVOISIER "On the Respiration of Animals" presented to the French Academy of Sciences in 1789 (*Oeuvres* II, pp. 688-703). It is a classic report in which scientific observations are interspersed with literary, philosophic and moral reflections, some of which, by giving a glimpse of troubled social conditions, seem almost prophetic of the outbreak of the French Revolution.

"In respiration, as in combustion, it is the atmospheric air which supplies oxygen and caloric; but, since in respiration it is the substance itself of the animal, *i.e.*, the blood, which supplies the combustible material, it follows that if animals do not con-

stantly regain by food what they lose by respiration, they will die just as a lamp goes out when its supply of oil is consumed" (Oeuvres de LAVOISIER, Vol. II, p. 691).

"The proofs of this identity of the effects of respiration and combustion are made immediately evident by experiment which shows that the air employed in respiration no longer contains, on leaving the lungs, the same quantity of oxygen. It has taken on not only carbonic acid but it contains much more water than it had before being respired. Now since vital air [*i.e.*, oxygen] can be converted into carbonic acid only by the addition of carbon and into water only by the addition of hydrogen, this double combination can be effected only by the vital air losing a part of its specific caloric. It follows, therefore, that the effect of respiration is to extract from the blood a part of its carbon and hydrogen and to leave there instead a portion of its specific caloric which, during the circulation of the blood, is distributed to all parts of the animal economy and produces that nearly constant temperature which is observed in all breathing animals.

"One might say that this analogy of combustion and respiration did not escape the attention of the poets or rather the philosophers of antiquity, of which they were the interpreters and spokesmen. That fire stolen from heaven, that torch of Prometheus, is not only an ingenious poetic conception but it is the faithful picture of the operations of nature, at least so far as concerns breathing animals. It might then be said with the ancients that the torch of life is kindled at the moment when the babe first breathes and that it is extinguished only at death" (Oeuvres, Vol. II, pp. 691-2).

"Our first experiments gave us some general ideas of respiration. We had even foreseen that it was accelerated during digestion and that animals consume then a greater quantity of air. We had likewise perceived that movement and exercise still further increased these effects, but we were still far from realizing the goal which we had set before us for after having worked with animals we desired to make experiments that relate more particularly to human respiration.

"However uncomfortable, however disagreeable, however dangerous even such experiments might be, M. SEGUIN desired that they should all be made upon himself. We have repeated them a large number of times and the accuracy of the results has almost always exceeded our expectations. The Academy has before it a part of the apparatus which we have used. We will give a detailed description of it in another memoir" (Oeuvres, Vol. II, p. 695).

"The experiments in which M. SEGUIN was the subject showed that a man fasting and at rest and at a temperature of 26° Réaumur consumes in an hour 1210 cubic inches [24 lit.] of oxygen; that this consumption is increased by cold, the same man, in the same state of fasting and at rest but at a temperature of only 12° Réaumur, consuming in an hour 1344 cubic inches [27 lit.] of oxygen. During digestion this consumption was increased to 1800 to 1900 cubic inches [36-38 lit.].

"Exercise increased all these figures considerably. While M. SEGUIN was fasting he lifted in a quarter of an hour a 15 lb. weight to a height of 613 feet. His consumption of oxygen during this period was 800 cubic inches or 3200 cubic inches [63 lit.] per hour.

"Finally the same sort of exercise during digestion raised the quantity of oxygen consumed to 4600 cubic inches [91 lit.] per hour. The work performed by M. SEGUIN in this period during a quarter of an hour was equivalent to lifting a 15 lb. weight to a height of 650 feet" (Oeuvres, Vol. II, pp. 695-6).

LUSK (1922) in referring to these results in his "History of Metabolism" made the following comment: —

"The *basal metabolism* was increased 10 per cent after exposure to cold; 50 per cent after taking food; 200 per cent by exercise; and 300 per cent on combining the influences of food and exercise. We now know more details and we may also calculate that LAVOISIER's determination of 24 liters of oxygen absorbed per hour in this first historical experiment on the basal metabolism was 25 per cent too high. As for the experimental plan, it is as modern as the work of to-day, and yet it was executed 140 years ago by the first man who really understood the significance of oxygen. It is only in the last decade that the summation of the individual stimuli caused by food and muscular work and noted by LAVOISIER has been verified. LAVOISIER also observed a con-

stant relation between the quantity of oxygen consumed and the rate of the pulse multiplied by the number of respirations.

"How LAVOISIER achieved these remarkable results is not known, for the times in which he lived became too troubled to allow further work in pure science. We find, however, the following statement in the original memoir: 'It would have been impossible to accomplish these exact experiments upon respiration before the introduction of a simple, easy and rapid method of gas analysis. This service M. SEGUIN has rendered to chemistry.'"

SEGUIN's improved method of gas analysis, referred to in this passage, consisted in the removal of oxygen from the air by means of burning phosphorus in an eudiometer tube over mercury. The carbonic acid was then absorbed by caustic potash solution. These improvements were a great advance over the older method of PRIESTLEY with nitric oxide.

In calculating the respective amounts of inspired oxygen that were used for carbon dioxide and water production, the procedure of LAVOISIER was to subtract the oxygen of the expired carbon dioxide from the total oxygen consumed and to apportion the remainder to water formation.

"Investigations of this character lead one to compare expenditures of energy between which there would seem to be no relationship. One might determine, for example, the foot-pounds of energy expended by a man in making a speech or by a musician in playing an instrument. One might even evaluate the mechanical work equivalent of the thoughts of a philosopher, of the writings of an author or of the score of a musical composer. Such operations, although considered as purely mental, have nevertheless a physical and material element which, when thus considered, permits one to compare them with the work of a laborer. It is therefore not without some justice that the French language employs the same word *travail* to designate both the work of the spirit and the work of the body, the *travail* of the study and the *travail* of the shop.

"From all of which it is evident that the quantity of oxygen consumed by different individuals is variable, and is never rigorously the same in any circumstance of life or at any moment of the day. However if one should wish to have a rough estimate of the average, or let us say, of the more usual amount of this consumption, it may be placed at about one cubic foot or 1728 cubic inches per hour which is equivalent to 24 cubic feet or 2 lbs. 1 ounce 1 gross in 24 hours . . ." (Oeuvres, Vol. II, p. 697).

"Thus far we have considered respiration only as a consumption of air, the same kind for the rich as for the poor; for air belongs equally to everyone and costs nothing. In fact the laboring man derives the greater benefit from this gift of nature. But now since experiment teaches us that respiration is a true combustion which consumes at each instant a portion of the substance of the individual, that this consumption is correspondingly greater as the circulation and respiration are accelerated and that it increases in proportion as the individual leads a more laborious and active life, a crowd of moral considerations are suggested from these findings of physical science.

"What fatality decrees that the poor man, who lives by the work of his arms and is forced to employ for his subsistence all the powers given him by nature, must consume more of himself than the sluggard who has less need of repair? Why the shocking contrast of a rich man enjoying an abundance which is not physically necessary for him but which is evidently of greater concern for the laborer? Let us be careful, however, not to blame nature and accuse her of faults that are undoubtedly the consequence of our social institutions and perhaps inseparable from them. Let us be content to bless philosophy and humanity which together give promise of wise institutions that will tend to bring about the blessing of equality, to increase the price of labor, to assure it a just recompense, and to offer to all classes of the poor more enjoyment and greater happiness. Let us above all resolve that the enthusiasm and exaggeration, which so easily influence men collected in large assemblies, and the human passions, which sway the masses so often against their own interest and engulf in their whirlpool the sage and the philosopher like other men, shall not overthrow a work undertaken with such fair prospects and do not destroy the hope of our country" (Oeuvres, Vol. II, pp. 698-9).

"We will close this memoir with a consoling reflection. It is not required, in order to merit well of humanity and to pay tribute to one's country, that one should participate in brilliant public functions that relate to the organization and regeneration of empires. The scientist, in the seclusion of his laboratory and study, may also perform patriotic functions; he can hope, by his labors, to diminish the mass of ills that afflict the human race and to increase its enjoyment and happiness; and should he, by the new paths which he has opened, have helped to prolong the average life of men by several years, or even by only several days, he can then also aspire to the glorious title of benefactor of humanity" (Oeuvres, Vol. II, p. 703).

Many questions of an agricultural chemical nature were referred to LAVOISIER by the Academy and his numerous well written reports upon such topics as the respiration of insects, plant nutrition, scarcity of cattle, penning of sheep, cultivation of clover, analyses of cloves and indigos, spoiled wheat and flour, distillation of spirits, manufacture of sugar, etc., etc., indicate not only the great extent of his practical knowledge of agriculture and industry, but the excellence of his judgment. In some of his reports it seems as if LAVOISIER with a sense of prevision had almost projected himself into the virulent polemics of a half century later, as for example in his discussion of a paper by SEGUIN upon the origin of the carbonaceous matter of crops.

"It seems natural at first to suppose that they draw it from the vegetable earth, the *humus*, the soil and the manure in which they grow. But this opinion presents a difficulty which seems insoluble for it is an established fact that various plants live in pure water and in air with apparently no substance in their environment available for supplying them with carbon. . . . It seems to follow from these experiments that it is not by the roots that carbon enters into the composition of plants. It remains to determine whether this substance, as seems quite possible, is not derived from the decomposition of the carbonic acid which surrounds plants" (Oeuvres, Vol. IV, pp. 536-8).

LAVOISIER's report, as executive member of the Saltpeter and Gunpowder Committee, on the construction and operation of nitre beds, on the soils naturally rich in nitre, on the determination of the quality of saltpeter, etc., also contains much of agricultural chemical interest.

Of great practical value was LAVOISIER's paper "Results of some agricultural experiments and reflections upon their relation to political economy" which was read in 1788 before the Paris Agricultural Society. In this address he describes some phases of the experimental work which he conducted upon his 300-acre farm at Blois. The very backward condition of agriculture in this district was attributed by LAVOISIER to the scarcity of cattle and the consequent lack of manure for fertilizing the fields. He thus describes the method which he adopted for improving his farm:—

"I realized after these considerations that the first thing to be done in regenerating my farm was to sow meadow land with grass and in general to increase the amount of forage for the livestock. This system of management being entirely new in that country, I had nothing to guide me. My neighbors were unable to teach me what crops were best for my soil or what kind of cultivation was most suitable for different crops. I was consequently obliged to make a large number of preliminary experiments and to study my fields before launching upon any extensive undertakings. Only after three years did I begin to realize that lucerne did not thrive in my fields and that it was almost impossible to protect it from a parasitic plant called *cuscutte* [dodder] which clings to it, multiplies and finally kills it; that my fields were better adapted for the culture of sanfoin, that clover did well in rainy years but often did not sprout in times of drouth; and finally that with care and by giving my fields adequate preparations

I could grow in regular rotation turnips and potatoes and upon fallowed land vetches and peas.

"With the results and observations of these preliminary years I was then able to commence carrying out the plan which I had first formed. From the beginning I introduced the practice of using folds, against which there existed and still exists in that neighborhood, a prejudice that only a long interval of time can overcome. Four to five hundred sheep, which I have kept in folds from midsummer to the end of October, give dung sufficient for 55 arpents [about 70 acres] without counting straw. This first operation enabled me to spread on 55 arpents the same quantity of dung that I was obliged formerly to distribute on 80 [about 100 acres]; that is to spread three loads per arpent in place of two.

"Since it is only with manure that one can increase the yield of straw on a farm and since at the same time it is only with straw that one can increase the manure, it will be seen that this double object can only be accomplished in slow progressive stages. I have hastened this progression by buying straw and by utilizing on my farm the straw of rented land. This straw, used as bedding, forage, etc., for the livestock which my sown grass land enables me to feed, has increased little by little the quantity of my manure and I have gradually raised the amount of this, in an interval of seven to eight years, from two to six or seven loads per arpent and I hope to reach ten and perhaps more in a few more years. The quantity of straw which I harvest has already almost doubled, but, what is remarkable, the yield of wheat per arpent has not increased appreciably or if it should show an increase in cases it is exceedingly small when compared with the gain in straw. Finally at the time I am writing (August 1787), I have about 25 arpents [about 32 acres] of good meadow grass, 2 arpents of turnips, 1 arpent of field beets, 1.5 arpents of potatoes, clover and vetch on fallowed land, a herd of 20 cows which I shall soon bring to 30, 500 sheep in folds and sufficient forage for at least 300 this winter. My barns and granaries are not large enough to store my crops; my yield of oats already exceeds my consumption" (*Oeuvres*, Vol. II, pp. 814-5).

LAVOISIER's agricultural enterprise was not undertaken for gain but for the purpose of making a large scale experiment in the praiseworthy effort to improve the ruinous state of French agriculture and to relieve the abject poverty of the peasants. The great expenses of these experiments, like those of his chemical laboratory, were defrayed from the lucrative profits of his vocation as farmer-general—profits wrung by a tragic irony from the very peasants and laborers whose conditions he strove to improve. To become a party to the iniquitous system of farming the nation's revenues caused LAVOISIER to lose the respect of some of his scientific colleagues and the commitment of this fatal blunder involved him finally in the terrible uprising which cost him his life. LAVOISIER's long experience as farmer-general gave him, however, a knowledge of the material wealth of France, such as few economists of his time possessed. His 60-page essay "*De la Richesse Territoriale du Royaume de France*" (1791) reveals a most intimate acquaintance with the agricultural and industrial resources of the French kingdom.

LAVOISIER's diversified interests in the fields of science, agriculture, industry, finance and economics required an enormous expenditure of intellectual effort. In addition to his exceptional scientific attainments and intuitive powers he possessed a high degree of administrative ability. His life although short was marvellously productive. Had he given more time to chemistry and less to other demands he would unquestionably have advanced the state of the science by several decades. He left many unsolved problems to which he alone possessed the clues.

The published works of LAVOISIER are of great interest to the historian of science for they give a detailed picture of the progress of a great chemical

genius in casting off erroneous conceptions and in advancing to correct conclusions. He was not a good mathematician and his results show occasional errors of carelessness and bad arithmetic. LAVOISIER was quick to see the implications of the chemical discoveries of his contemporaries and did not hesitate to weave them into his own experiments but in so doing he was sometimes neglectful about making the proper acknowledgments. Always jealous of his own claims of priority he was at times strangely indifferent about the rights of others.

LAVOISIER took a leading part in devising the system of chemical nomenclature which is the basis of that used today. This much-needed reform was second only to the one that he accomplished in overthrowing the doctrine of phlogiston.

The work of LAVOISIER may be summarized by saying that he brought into chemistry a new doctrine, a new nomenclature, a new outlook, and a new spirit. His reforms in the various branches of inorganic, organic, physiological, and agricultural chemistry mark the commencement of the modern era.

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Albrecht Daniel Thaer (1752-1828) and Heinrich Einhof (?-1808):—The work of ALBRECHT THAER, the eminent German writer upon husbandry, and that of his associate HEINRICH EINHOF, a pioneer agricultural chemist, are so closely interwoven that their contributions to the chemistry of agriculture must be considered together.

THAER was born at Celle, the son of a physician to the court of the King of Hannover. At the age of 18 he entered Göttingen University to study medicine. After obtaining his doctor's degree he returned to Celle and on

his father's death in 1778 succeeded him as Court practitioner. In 1784 he became a member of the Royal Agricultural Society at Celle and the love of husbandry, thus stimulated, began gradually to wean him from his practice of medicine. He bought an estate near Celle, erected buildings and devoted all his leisure to agricultural research. He developed a system of field rotation by means of which he greatly increased the yield of his crops. This reform attracted the wide attention of farmers and his flood of writings on agricultural subjects still further enhanced his reputation.

Although appointed physician in ordinary to GEORGE III, King of England and Hannover, THAER continued to curtail his medical practice. In 1802 he converted his estate into an agricultural institute, the first of its kind, where he gave lectures on farming. THAER appointed EINHOF to assist him in this educational enterprise by teaching the applications of chemistry, physics, and mineralogy to agriculture. Many future specialists, among them CARL SPRENGEL, obtained their first instruction in the theory and practice of agriculture at THAER's institute. In 1804 THAER accepted a call by King FRIEDRICH WILHELM III of Prussia, who among other privileges made him a Privy Councilor, a Member of the Berlin Academy of Sciences and the head of a new State Agricultural Institute, which THAER established at Möglin.

EINHOF, who had received an appointment as professor at the new institute, accompanied THAER to Möglin but his promising career as an agricultural chemist was unfortunately cut short by death in March, 1808. His analytical memoranda and other unpublished data were assembled and edited by THAER who published them first in the 7th and 8th volumes of his "*Annalen des Ackerbaues*" (*Annals of Agriculture*). They also appeared in book form as HEINRICH EINHOF and ALBRECHT THAER's "*Grundriss der Chemie für Landwirthe*" (*Outlines of Chemistry for Farmers*, Berlin, 1808), a work which was frequently mentioned by DAVY and other later writers.

Much of EINHOF's work appears also in the pages of HERMBSTÄDT's "*Archiv der Agriculturchemie*" and of ALBRECHT THAER's "*Grundsätze der rationellen Landwirthschaft*" (*Principles of rational Husbandry*, 4 vols., Berlin, 1809-12), a work of vast influence which was widely translated. THAER's book greatly helped, especially in the sections devoted to Manure, Fodder, and Cattle; to Cultivation and Crop Rotation; and to Agronomy, in arousing an interest in the important relations of chemistry to agriculture. Indeed the 230 pages of this work (Vol. II, pp. 43-272) devoted to Agronomy, with its discussion of the chemistry of soils, manures, and fertilizers, might be considered as a separate treatise upon this particular department of agricultural chemistry. It is to Vol. II of THAER's "*Grundsätze*" that subsequent page references pertain.

As always happens in the development of a science, many untenable hypotheses were being continually advanced even by the leading writers upon the relations of chemistry to agriculture. This was unavoidable and in no sense a detraction from the merits of the great men who, hampered by false traditions and by imperfect apparatus and analytical methods, were trying to grope their way out of an almost impenetrable wilderness

of doubt and ignorance. The old alchemistic doctrine of the transmutability of the elements appears, for example, in the books of THAER, who although generally a careful thinker, favored the idea that lime might be converted under certain conditions into silica (p. 56). Because EINHOF and other analysts found much lime in the ash of certain plants that grew in soil apparently deficient in lime, THAER concluded that lime must have been metamorphosed within the plant. He suggested that this lime may have come from the potash since potash had been found to prevail in the ash when the plant was incinerated in the green state but lime was found to be the more abundant when the incineration was performed upon the dry material of the same plant (pp. 49-50). Erroneous conclusions of this character, due to mistakes of observation and to faulty experimental technique, appear in many publications of this period.

As the student reviews the developments in the history of agricultural chemical science, he is repeatedly impressed by the slowness and apparent reluctance of investigators to revise their opinions even long after the time when the unreliability of their views had been demonstrated and exposed. THAER, although referring constantly to DE SAUSSURE'S "Chemical Researches on Vegetation", completely ignored DE SAUSSURE'S views on the non-transmutability of the mineral constituents of plants and on the inadequacy of humus as a plant food. He preferred to accept SCHRADER'S view that potash, lime, silica, etc., were actually generated in the plant, while as regards humus he held that the fertility of soils is wholly dependent upon this constituent (p. 107).

THAER estimated humus by determining the loss in weight that a soil underwent on ignition and applied this highly imperfect method to a tabular classification in which the productivity of soils was rated according to their humus content. While a deficiency of humus in soils is highly detrimental THAER held that an excess was equally injurious and he constantly inculcated the doctrine of avoiding too much and too little of this, that, or the other (a favorite doctrine also of THAER'S pupil SPRENGEL).

The most productive cultivated soil noted by THAER was on the right bank of the lower Elbe (p. 123). It contained 11.5 percent humus, 4.5 percent lime and a remaining 84.0 percent that consisted largely of clay. In his descriptions of sandy, clayey, loamy, humus and other types of soils THAER laid especial stress upon the optimum balance of their physical properties such as stiffness, dryness, porosity, temperature, etc., a deficiency or excess of any quality being regarded as injurious. He was thus among the first to emphasize the importance of physical considerations, a branch of soil science that was not seriously developed until two decades later by SCHÜBLER.

In the section of his book devoted to fertilizers THAER, as elsewhere, is much sounder in practice than in theory. He gives careful directions for the care of barnyard manure, composting, preparation of lime, employment of marl and other technical operations, but in his attempts to explain the chemical action of these he usually wandered far astray. His views on the fertilizing power of dead plant and animal remains represent a type of vitalistic philosophy that prevailed for several decades in the early nineteenth century and survivals of this philosophy still exist. According to THAER

"Humus forms a more or less important constituent of the soil. The productivity of the soil depends entirely upon it, for excepting water it is the only substance in the soil that gives nutriment to plants. It is the dark residue of plant and animal decay; in the dry condition it is a dusty and in the moist condition a soft fatty-feeling powder. According to the different nature of the substances from which it was derived and according to the conditions under which the putrefaction or decay of these substances took place, humus is of a varying character; it has however certain common properties and is essentially the same product. It is a representation of organic force, a compound of carbon, hydrogen, nitrogen and oxygen, such as cannot be produced by inorganic natural forces, those elements in dead nature forming only binary combinations. Accompanying these more abundantly occurring elements of humus there occur a few others in smaller amounts, as phosphorus, sulfur, a little active earth and sometimes different salts.

"As humus is a product of life, it is also a condition of life. It gives nutriment to the organism. Without it no individual living thing, at least of the higher animals and plants, can be supposed to exist on the face of the earth. Death and decay are therefore absolutely necessary for the preservation and generation of new life. The more there is of life, the more humus is produced and the more of humus there is produced, the more food is supplied to the living organism. Every living organism during its existence assimilates more and more of nature's raw materials, which are finally resolved into humus, so that this substance accumulates in greater amount, the more men and animals there are in a given region and the more we strive to increase the productivity of the soil, provided we do not carelessly permit it to be carried away by water into the ocean or to be destroyed by fire. We can follow the history of humus from the beginning of the world if we only study the progressive steps of vegetation on bare rocks. First lichens and mosses develop, in whose remains higher plants find nutriment; the latter by their decay still further increase the mass of dead materials until finally a deposit of humus is laid down sufficient to support the growth of the strongest trees" (pp. 107-8).

This purely vitalistic conception of the manurial value of dead plant and animal matter was extended by THAER even to the ashes of such materials which he supposed to have a greater fertilizing action than an equivalent amount of potash, lime, etc., of purely inorganic origin. In this connection he remarks:—

"There is probably in the ash still a remnant of vegetable life which our sense perceptions are unable to detect. This idea seems to be confirmed by the almost general observation that ashes produced by a slow combustion and by a more limited access of air are far more active as a fertilizer than when obtained at a high heat" (p. 268).

We now attribute any deficiency in the fertilizing value of plant ashes prepared at a high temperature of ignition to volatilization of potash or to the lower assimilability of the potash in the vitrifications produced by its fusion with silica.

As to the function of the elementary constituents of fertilizers in a plant physiological sense THAER had only a faint conception. He knew that horse dung, urine and other animal excreta evolved ammonia and supposed that this alkaline emanation, when manure was thoroughly incorporated with the soil, had a favorable action by rendering undecomposed humus more soluble. He held that manure should be allowed to ferment within the soil, and not in piles, in order that the heat evolved might have a beneficial warming effect on the growth of crops.

Of mineral fertilizers THAER discusses the application of lime, marl, gypsum, saltpeter and various other inorganic salts. He held that lime should be applied only in a fine well-slaked condition and then only to

fallow soils. To obtain its best effect lime must be intimately mixed with the soil by repeated harrowing. THAER attributed its beneficial action in small part to its ability to attract carbon dioxide and then give this off as nutriment to the crop but chiefly to its power of converting humus and unresolved vegetable matter into easily assimilable plant food (p. 238). The latter opinion, held also by DAVY, prevailed for many decades. The current opinion that lime helped to eradicate weeds was also emphasized by THAER. "A weak application is valueless; an excess injures the soil by forming cement-like concretions" (p. 242).

THAER devotes twelve pages of his treatise to the use of marl which he defines as an intimate mixture of clay and carbonate of lime in varying proportions. Its beneficial action is twofold—first physical by the action of the clay in improving the texture of porous soils and second chemical by the action of the lime. The physical action is permanent, the chemical benefit, however, is slowly exhausted and is not usually noticeable after ten to twenty years. THAER regarded marl as the most available, the most beneficial and the most pronounced and lasting in its action of all soil amendments (pp. 246–58).

The introduction of gypsum as a fertilizer is accredited by THAER to the writings of the clergyman, MAYER, who greatly extolled its virtues about the middle of the eighteenth century. Its use then extended to France and to America but not to England; a fact that THAER suggests may be due to the prejudice of the English against everything French or German! Gypsum is more beneficial on dry than on wet soils. Its favorable effect is most pronounced with leguminous crops and is explained by its probable inter-reaction with humus by which carbon dioxide is produced together with a new compound of rapid assimilability, "the nature of which we do not yet know and perhaps, because of its speedy decomposition, never will know" (pp. 260–4). Other fanciful speculations of THAER upon the chemical action of fertilizers are passed over.

The parts of THAER's "Principles of rational Husbandry" relating to farm management, rotation and culture of crops, rationing of cattle, utilization of farm produce, farm machinery, reclamation of land and other topics are filled with much practical information of great value to the farmer. They do not deal with chemical details and for such considerations THAER refers his readers to the publications of EINHOF.

It was EINHOF's great service by means of many painstaking analyses to enlarge the knowledge of the chemical composition and feeding value of different crops and crop constituents. His results, which were extensively quoted by DAVY and other writers, are based upon the number of grains of ingredient in an eight ounce (3840 grains) or sixteen ounce (7680 grains) sample. EINHOF's analysis of barley meal is cited as an example (DAVY, pp. 125–6):—

	GRAINS PER 8 OZ. SAMPLE	RESULTS RECALCULATED TO PERCENTAGE BASIS
<i>Volatile matter</i>	360	9.38
<i>Albumen</i>	44	1.15
<i>Saccharine matter</i>	200	5.21
<i>Mucilage</i>	176	4.58
<i>Phosphate of lime, with some albumen</i>	9	.23
<i>Gluten</i>	135	3.52

<i>Husk, with some gluten and starch</i>	260	6.77
<i>Starch, not quite free from gluten</i>	2580	67.19
<i>Undetermined and loss</i>	76	1.97
TOTAL	3840	100.00

THAER's fame as an agricultural authority rested chiefly upon his reformed system of husbandry, his improvement in the breed of Merino sheep for wool production and his work as a teacher and author. For these accomplishments he received many decorations, appointments and other honors. He was appointed a professor at the newly created University of Berlin and his agricultural school at Möglin was raised to the status of a Royal Academy. THAER's prominence, however, had an unfortunate influence on contemporary agricultural chemistry in that his doctrines regarding vitalism, transmutability of mineral elements, and the nutrient value of humus obtained a much wider circle of adherents than would otherwise have been the case. THAER's opinions on these subjects prevailed over those of DE SAUSSURE until they received their final overthrow by LIEBIG.

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Jean Antoine Claude Chaptal (1756-1832):— The awakening of interest in agricultural chemistry in all its varied practical, industrial, and economic aspects is due chiefly to the celebrated French chemist, J. A. C. CHAPTAL. His international reputation as a chemical technologist, agriculturalist, economist, and statesman, both during and after the Napoleonic era, caused all his works, which passed through many editions and translations, to be widely read.

CHAPTAL was born, the son of an apothecary, at Nogaret in the department of Lozère in southeastern France. After completing his primary education at Mende, he entered the School of Medicine at Montpellier where he obtained his first instruction in chemistry. In 1777 he went to Paris to continue his chemical studies but was recalled to Montpellier in 1781 to accept the professorship of chemistry newly founded by the States of Languedoc. He was among the earliest to teach the new doctrines of LAVOISIER. On the death of a rich uncle he inherited considerable wealth with which he established chemical works for the manufacture of acids, alum, soda and other substances in Montpellier.

The publication of a political pamphlet during the Revolution led to CHAPTAL's arrest but more fortunate than LAVOISIER he was soon set at liberty. His success in the management of chemical works led to his appointment in 1793 by the Committee of Public Safety as manager of the

important saltpeter works at Grenelle. In 1799 NAPOLEON made him a councilor of state and in 1801 minister of the interior. In the latter capacity he founded a school and conservatory of arts (now a great museum), reorganized the hospitals, began the canalization of France, encouraged manufactures, introduced the metric system of weights and measures and inaugurated other reforms, in recognition of which NAPOLEON conferred upon him the title of Count of Chanteloup. A disagreement with NAPOLEON caused his temporary retirement in 1804 but he was soon recalled and afterwards made director-general of commerce and manufactures and a minister of state. After NAPOLEON's downfall CHAPTAL withdrew to private life and devoted his remaining years to the management of his estate and to the writing of his "De l'industrie française" (2 vols. 1819) and "Chimie appliquée à l'agriculture" (2 vols. 1823). He died at Paris on July 30, 1832, rich in honors and in the affection of his people. The following estimate of CHAPTAL's character was given by THENARD in a eulogy before the French Academy:

"He was endowed of a kind heart, of a mild and gentle character, moderate in tastes and opinions, full of benevolence towards every one, of affectionate regard for his associates, of devotion to his friends; ready to confer a favor when in his power and doubling it with the grace by which he conferred it; unhappy when compelled to refuse, and always softening the refusal by expressions which showed the goodness of his heart."

CHAPTAL had always shown a great interest in agriculture and devoted Part Four of his "Éléments de Chimie" to plant and animal chemistry. This work which was translated into German by HERMBSTÄDT and into Italian and Spanish extended the influence of CHAPTAL's chemical teachings into many countries. As in all his later works the practical applications of chemistry are chiefly emphasized. This is indicated in the following passage from the preface (CHAPTAL 1801, p. xviii).

"I publish these elements of Chemistry with the greater confidence, because I have had opportunities myself of observing the numerous applications of the principles which constitute its basis to the phenomena of nature and art. The immense establishment of chemical products which I have formed at Montpellier, has allowed me to pursue the development of this doctrine, and to observe its agreement with all the facts which the various operations present to us. It is this doctrine alone which has led me to simplify most of the processes, to bring some of them to perfection, and to rectify all my ideas. It is therefore with the most intimate confidence that I propose it."

In the Preliminary Discourse of his "Elements of Chemistry" CHAPTAL emphasizes the importance of the applications of chemistry to agriculture (*loc. cit.*, pp. xl-xliii).

"Agriculture is more intimately connected with chemistry than is usually supposed. It must be admitted that every man is capable of causing ground to bear corn; but what a considerable extent of knowledge is necessary to cause it to produce the greatest possible quantity! It is not enough, for this purpose, to divide, to cultivate and to manure any piece of ground: a mixture is likewise required of earthy principles so well assorted, that it may afford a proper nourishment; permit the roots to extend themselves to a distance, in order to draw up the nutritive juices; give the stem a fixed base; receive, retain, and afford upon occasion, the aqueous principle, without which no vegetation can be performed. It is therefore essential to ascertain the nature of the earth, the avidity with which it seizes water, its force of retaining it, &c.; and these

requisites point to studies which will afford principles not to be obtained by mere practice but slowly and imperfectly.

"Every grain requires a peculiar earth. Barley vegetates freely among the dry remains of granite; wheat grows in calcareous earth, &c. And how can it be possible to naturalize foreign products, without a sufficient stock of knowledge to supply them with an earth similar to that which is natural to them?

CHIMIE

APPLIQUÉE

A L'AGRICULTURE,

PAR M. LE COMTE CHAPTAL,

PAIR DE FRANCE, CHEVALIER DE L'ORDRE ROYAL DE SAINT-MICHEL, GRAND-OFFICIER DE LA LÉGIION-D'HONNEUR, MEMBRE DE L'ACADÉMIE ROYALE DES SCIENCES DE L'INSTITUT DE FRANCE, DE LA SOCIÉTÉ ROYALE ET CENTRALE, ET DU CONSEIL ROYAL D'AGRICULTURE, ETC., ETC., ETC.

TOME II.

Th. de Saussure.

A PARIS,

CHEZ MADAME HUZARD, IMPRIMEUR-LIBRAIRE.

RUE DE L'ÉPERON, N°. 7.

1823.

FIG. 26. — Title page of CHAPTAL's "Chimie appliquée à l'Agriculture," Vol. II, Paris, 1823, with autograph signature of TH. DE SAUSSURE.

"The disorders of grain and forage, and the destruction of the insects which devour them, are objects of natural history and chemistry: and we have seen in our own times the essential art of drying and preserving grain, and all those details which are interesting in the preparation of bread, carried by the labours of a few chemists to a degree of perfection which seemed difficult to have been attained.

"The art of disposing stables in a proper manner, that of chusing water adapted for the drink of domestic animals, the economical processes for preparing and mixing

their food, the uncommon talent of supplying a proper manure suited to the nature of soils, the knowledge necessary to prevent or to repair the effects of blights—all come within the province of chemistry and without the assistance of this science our proceeding would be painful, slow, and uncertain.

"We may at present insist upon the necessity of chemistry in the various branches of agriculture with so much the more reason, as government does not cease to encourage this first of arts by recompences, distinctions, and establishments; and the views of the state are forwarded by the proposal of means to render this art flourishing. We see, with the greatest satisfaction, that, by a happy return of reflection, we begin to consider agriculture as the purest, the most fruitful, and the most natural source of our riches. Prejudices no longer tend to oppress the husbandman. Contempt and servitude are no longer the inheritance received for his incessant labours. The most useful and the most virtuous class of men is likewise that whose state is most minutely considered; and the cultivator of the ground in France is at last permitted to raise his hands in a state of freedom to Heaven, in gratitude for this happy revolution."

In the 149 pages of his "Elements" that are devoted to Vegetable Chemistry CHAPTAL discusses first the nutritive principles of plants in which he considers water, earth, nitrogen, carbonic acid, and light. The organic and mineral components of plants, such as mucilage, fixed and volatile oils, resins, balsams, starch, gluten, sugar, acids, coloring principles, ligneous matter, mineral constituents, etc., are then described with special reference to their properties, extraction, and utilization. The alterations that vegetable substances undergo as a result of fermentation, putrefaction, destructive distillation, etc., are also considered. In the remaining 88 pages of the "Elements" devoted to Animal Chemistry, the chemical properties of milk, blood, fat, bile, muscle, urine, etc., are reviewed, the preparation of phosphorus from urine and bones is described and the constituents obtained from quadrupeds, fishes, birds, insects, etc., that are of use in medicine and the arts are considered.

The great popularity of CHAPTAL's "Elements of Chemistry" is largely due to his interesting anecdotal treatment of the subject. Several hundred authorities are cited and the copious references to previous literature are of great value to historical students. Although the work is largely a compilation of pre-existing knowledge, CHAPTAL as everywhere shows a characteristic independence of opinion as for example in his preference (*loc. cit.*, p. xxxv) of the word Nitrogen in place of the term Azote introduced by the authors of the New Nomenclature and still employed by French chemists.

None of CHAPTAL's later works exercised so wide an influence as his "Chimie appliquée a l'Agriculture" (Chemistry applied to Agriculture). While he made no attempt to formulate a definite system of agricultural chemistry, his numerous illustrations of the applications of chemistry to the varied operations of farms and estates, drawn largely from his own extensive experience, caused men to take a vastly wider conception of the term agricultural chemistry than had previously been held. This is made evident by a synopsis of the chapter headings of his book, as taken from the first American translation (Boston 1835-6):—

"1, General Views of the Atmosphere, considered in its Effects upon Vegetation; 2, The Nature of Earths and their Action upon Vegetation; 3, The Nature and Action of Manures; 4, Germination; 5, The Nourishment of Plants; 6, Improvement of the Soil; 7, The Succession of Crops; 8, The Products of French Agriculture; 9, The Nature and Uses of the Products of Vegetation (Gum, Starch, Sugar, Wax, Oils,

Resin, Fibre, Gluten and Albumen, Tannin, Vegetable Acids, Fixed Alkalies); 10, The Preservation of Animal and Vegetable Substances (by drying; by excluding air as in siloing and canning; by treating with salt, spirituous liquors, smoke, sugar, etc.); 11, Milk and its Products (Cream, Butter, Cheese); 12, Comparison between an Agricultural and a Manufacturing Nation; 13, Large and Small Estates; 14, The Encouragement which should be given by the Government to French Agriculture; 15, Fermentation; 16, Distillation; 17, Means of Preparing wholesome Drinks for the Use of Country People; 18, Farm Buildings, both for Men and Animals, and the means of making them healthful; 19, Washing, Bleaching, etc.; 20, Cultivation of Woad and the Extraction of Indigo from it; 21, Cultivation of the Beet Root and the Extraction of Sugar from it (Cultivation; Extraction; Refining; Distilling molasses; Products and By-products; Costs of Installation; Etc.)."

It will be noted that CHAPTAL does not limit his discussions to the chemistry of the atmosphere, soils, fertilizers and plant growth, as was done by DAVY and most previous writers upon agricultural chemistry, but that he enormously amplifies the scope of his volume by making these subjects, which are treated in the first seven chapters, an introduction to the main practical part of his book contained in the fourteen remaining chapters. He discusses the technological processes involved in the preparation of vegetable and animal materials that are produced upon the farm such as gum, starch, sugar, wax, fixed and volatile oils, resin, vegetable fibres, wood, charcoal, albumen and gluten, flour, tannin, leather, vegetable acids, vinegar, and potash. The operations of cooking; food preservation; fermentation of wine, cider, and beer; alcohol distillation; butter and cheese manufacture; preparation of fruit juices and other beverages; purification of water; farm sanitation; washing and cleaning of fabrics; indigo fabrication; and beet sugar manufacture; are all described with a wealth of historical references and personal observations which were the results of CHAPTAL'S immense learning and long years of practical experience. His chemical and technological discussions are interspersed with philosophical reflections upon national and international economics, upon the comparative merits of large and small estates, upon public health and morality and numerous other subjects which in their broad significance are as pertinent today as they were a century ago.

CHAPTAL'S practical outlook and modest estimation of his own work are indicated in the following quotation from his preface (Amer. edit. 1835-6, pp. xxxviii-xl): —

"This work is not perfect, and I can myself judge of its imperfections better than any one else; but, such as it is, I believe it will be found useful. I trust that the application of the physical sciences to agriculture will be extended in proportion as those sciences advance; and that a more thorough knowledge of the principles according to which they act, will occasion the rectification of any errors which may have arisen from their having been misapplied. The celebrated DAVY, of England, has already published a work upon Agricultural Chymistry, from which I have borrowed many excellent principles: others will do better than we have done.

"Hitherto the physical sciences have been applied to the other arts much more than to agriculture; many arts have, in our day, been originated or improved, by their means, whilst the progress made in agriculture has been very trifling. This difference appears to me to proceed from two causes: the first of which is, that the greater part of the phenomena offered to us by agriculture are the effects of the laws of vitality, which govern the functions of plants, and these laws are still unknown to us; whilst, in the arts which are exercised upon rude and inorganic matter, all is regulated, all is produced, by the action either of physical laws only, or of simple affinity, which are

known to us. The second cause is, that in order to apply the physical sciences to agriculture, it is necessary to study their operations profoundly, not only in the closet, but in the fields.

"Though the proprietor of a large domain, of which I have for a time directed the labors, I feel that the facts which I have been able to collect upon various subjects, are still insufficient for the establishment of indisputable principles regarding them; and in all such cases, I have done nothing but present to the reader the doubts or the simple probabilities which may have arisen from my observations. I may have committed many errors in my explanations, but I believe I have not misstated a single fact; and it is in this belief that I offer this work to the agriculturist."

For promoting the principles set forth in his "*Chimie appliquée à l'agriculture*" CHAPTAL advocated the establishment in France of experimental schools of husbandry each with a professor upon the applications of chemistry to agriculture.

CHAPTAL's "Chemistry applied to Agriculture" although written for the purpose of improving agricultural conditions in France, was immediately translated into German by EISENBACH under the title, "*Agriculturchemie von Graf CHAPTAL*" (Stuttgart 1824) and thereby exerted in the next few years a considerable influence in German agricultural circles. The work had also a great popularity in the United States. A first American translation of the second French edition was published at Boston in 1835-6. Extracts from this translation "On the Cultivation of the Beet Root and the Extraction of Sugar therefrom" began to be published in July 1836 in the *New England Farmer* and were continued through seven issues of this weekly periodical. CHAPTAL's book gave a great stimulus to sugar beet growing in the United States in the late eighteen thirties. Many American farmers, taking CHAPTAL as their guide, began to make beet sugar on a small experimental scale, but a full half century had yet to elapse, with many trials and failures, before an American beet sugar industry became an established fact.

CHAPTAL's great service to agricultural chemistry consisted in calling attention to the importance of chemistry in the hitherto neglected technological operations that are conducted upon large farms and estates. While such operations are secondary to the study of the composition and mutual chemical relationships of soils, fertilizers, crops and farm animals, they nevertheless constitute a legitimate part of the field of agricultural chemistry and one that students of this science cannot afford to ignore. CHAPTAL was also the strongest advocate that agricultural chemistry has ever had as regards its importance to the economic welfare and prosperity of a nation.

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on the use of lime as a manure by M. PUVIS, with introductory observations to the same by JAMES RENWICK. Translated and edited by William P. Page, New York.

Sigismund Friedrich Hermbstädt (1760-1833):— One of the first German chemists to adopt the new reforms of LAVOISIER was S. F. HERBSTÄDT. He was born at Erfurt where he attended the local gymnasium and university and began the studies of medicine and chemistry. Later he moved to Berlin where he conducted a pharmacy and continued his studies at the Medico-Surgical College to which he was appointed professor of chemistry and pharmacy in 1791. He held the offices of Royal Apothecary, Sanitary Commissioner and Privy Councilor and in 1803 was elected a member of the Berlin Academy of Sciences. In 1810 he was appointed professor of technology at the University of Berlin, in which position he continued until his death.

HERBSTÄDT was an indefatigable writer. He translated the works of LAVOISIER into German and his own "Systematischer Grundriss der allgemeinen Experimental-Chemie" (Systematic Basis of General Experimental Chemistry) (3 vols. 1791) helped greatly to extend the new chemical philosophy. He published numerous works upon chemical technology, many of which relate to the industrial utilization of agricultural products, including such subjects as tanning, soap making, beet-sugar manufacture, conversion of starch into sirup and sugar, distillation of brandy, and beer-brewing. In addition to his other numerous literary activities HERBSTÄDT was also editor of various technological journals. Agricultural chemists will remember him also from the fact that he was the earliest to employ the designation "Agricultural Chemistry" and was the first to found a journal devoted to this science. This was his "Archiv der Agriculturchemie" or, to give the English translation of its complete title, "Archives of Agricultural Chemistry for intelligent Farmers, or a Collection of the most important Discoveries, Experiences and Observations in the field of Physics and Chemistry for discerning Farmers, Owners of Estates and Friends of economic industrial Pursuits". This periodical, of which seven volumes appeared at irregular intervals between 1803 and 1818, had a long list of distinguished contributors from all parts of Europe (including such scientists as ALEXANDER VON HUMBOLDT in Germany, SMITHSON TENNANT in England, ANTOINE PARMENTIER in France and THÉODORE DE SAUSSURE in Switzerland) whose articles, upon the relations of chemistry to soils, fertilizers, composition of crops, growth of vegetables, germination of seeds, manufacture of cheese and numerous other subjects, are indicative of the growing realization of the immense scope of agricultural chemistry.

The difference in meaning between "Agricultural Chemistry" and other designations such as "Relations of Chemistry to Agriculture", "Chemistry as Applied to Agriculture", "Chemical Foundations of Agriculture", etc., may appear trivial, yet there is a distinction of real significance for a branch of chemistry is now set off for the first time as being peculiar to agriculture. The terms "Agricultural Chemistry", "Metallurgical Chemistry", "Medical Chemistry" and other similar loosely applied designations, seem to have been selected originally as short convenient expressions to cover a borderland where several fields of science overlap. The term "Physical Chemistry", to indicate a field where physics and chemistry are both in-

volved, had been introduced as early as 1715 by STAHL and analogous designations began to be applied later with the advancement of chemical knowledge. Other sciences, however, besides chemistry, such as physics, geology, mineralogy, meteorology, biology, plant and animal physiology, technology, etc., enter into the same borderland that was marked off by the early writers as "Agricultural Chemistry" and hence arose the confusion which in later times was the cause of so much misunderstanding. HERBSTÄDT in the optional title of his "Archiv der Agriculturchemie", viz., "Sammlung der wichtigsten Entdeckungen, Erfahrungen, und Beobachtungen in der Physik und Chemie für rationelle Landwirthe, Güterbesitzer und Freunde der oekonomischen Gewerbe", indicated in fact that his new periodical was devoted as much to the physics as to the chemistry of agriculture. He might with equal justice have mentioned biology, physiology and other natural sciences.

In the first volumes of "Archiv der Agriculturchemie" HERBSTÄDT published a series of popular articles upon the fundamentals of chemistry in their relation to agricultural practice for the purpose of presenting to lay readers a fairly complete system of "agricultural chemistry in a nut shell" (*Agriculturchemie in nuce*). These articles might be considered as chapters of an elementary treatise upon agricultural chemistry and they were most useful in quickening an interest in the subject among young students and the general public. The important relationship of agricultural chemistry to the national welfare was also recognized by HERBSTÄDT who in Vol. 1 of his "Archiv" (p. 121) published a German translation of LAVOISIER's "Results of some Agricultural Experiments and Observations upon their Relation to Political Economy" with a fine tribute to the great French chemist.

HERBSTÄDT's "Archiv" served also a most useful purpose in publishing the results of original investigation, among which were several important articles by the famous German agricultural writer, ALBRECHT THAER, and his chemical associate, HEINRICH EINHOF.

HERBSTÄDT devoted much of his own time to agricultural chemical research and was one of the earliest to make large-scale field experiments. His investigations upon the chemical composition of crops, more especially cereals, and the influence of fertilizers on the production of the proximate constituents of plants cover a period of nearly two decades from 1815 until his death. An epitome of these experiments, which relate to subjects of present-day interest, is contained in Volume 12 (1831) of ERDMANN's "Journal für technische und oekonomische Chemie" (pp. 1-53).

Among the questions which HERBSTÄDT proposes for consideration are the following: (1) Do the nutritive elements of fertilizers reappear in the organs of plants? (2) Do these elements participate in the formation of such organs and of the plant constituents deposited therein? (3) Can the quantity of each plant constituent be increased by increasing the amount of the elements adapted for its formation? (4) Can we determine by experiment whether a given cereal, cultivated for years in succession on the same field, without addition of new fertilizer, suffers a decrease in yield with each year and whether by a rotation with other cereals or better with seed crops, roots, tubers, etc., a better yield of grain can be obtained without adding new fertilizer?

In his attempt to solve these questions HERMBSTÄDT planted different cereals in plots that were fertilized with the manure of different farm animals, urine, animal blood, etc., and determined the amount of fiber, gluten,

A r c h i v
der
Agriculturchemie
für
denkende Landwirthe,
oder
S a m m l u n g
der wichtigsten Entdeckungen, Erfahrungen und
Beobachtungen
aus
dem Reiche der Physik und Chemie
für
rationelle Landwirthe, Güterbesitzer, Forstmänner
und Freunde der ökonomischen Gewerbe.

Herausgegeben

von

D. Sigism. Friedrich Hermbstädt,
Königl. Preussischen Geheimen Raths etc.

Ersten Bandes zweites Heft.

(Mit dem Bildniß des Herrn Geheimen Raths Thaer.)

Berlin, 1804.

In der Realschulbuchhandlung.

FIG. 27 — Title page of HERMBSTÄDT'S "Archiv der Agriculturchemie", Berlin, 1804. The first journal devoted to agricultural chemistry.

starch, fat, albumen, sugar, gum, phosphates, etc., in the grain from such plots and from check plots that were unfertilized. The results showed that the fertilized plots gave higher yields of grain than the unfertilized and that the kind of fertilizer seemed to have a marked influence on the composition

of the grain. The parts of gluten and starch in 5000 parts of wheat varied from 1755 gluten and 1995 starch in the plot fertilized with human urine to 598 gluten and 4117 starch in the plot fertilized with cow dung. The wheat from the unfertilized plot gave 460 gluten and 3333 starch. The gluten results in these and the other experiments were obviously vitiated by inherent errors of analysis and technique. HERMBSTÄDT concludes that fertilizing cereals with manures of high nitrogen content increases the amount of gluten and that fertilization with manures of high carbon content increases the amount of starch in the grain. He recommended, therefore, the selection of fertilizer according to the requirements of the industry that used the grain, the baker for example needing a grain high in gluten and the starchmaker, brewer and distiller a grain high in starch.

HERMBSTÄDT's purpose in conducting these experiments was a laudable one, but the experimental and analytical technique of his time was too undeveloped to permit of their successful performance. The supposition that increasing the carbon content of a fertilizer could increase the starch content of the crop is a fallacy that owed its origin to the humus theory of plant nutrition. It has been the usual history of agricultural chemical research that, with the acquisition of new knowledge, a great part of the experimental conclusion of one generation has been revised or rejected by the next.

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(Nicolas) Théodore de Saussure (1767-1845): — It was LAVOISIER who chiefly helped to provide the foundation stones of modern agricultural chemistry but it was THÉODORE DE SAUSSURE who put them in place. The fruitful results of the new chemistry are revealed no where more brilliantly than in his works.

He was born at Geneva, the eldest son of HORACE BÉNÉDICT DE SAUSSURE (1740-99), celebrated Swiss naturalist and Alpine explorer. The elder DE SAUSSURE was a versatile scientist and well grounded in physics, chemistry, geology, and meteorology. He devised hygrometers, eudiometers, and other high precision apparatus in the use of which he trained his son who accompanied him on his various expeditions. Young DE SAUSSURE was attracted to chemistry by the work of LAVOISIER and his special interest in experimental plant chemistry was stimulated by the work of PRIESTLEY, INGEN-HOUSZ, and SENEBIER.

DE SAUSSURE's first paper on the density of air at different altitudes was published in 1790 but his first contribution on plant chemistry, "Is the formation of carbonic acid essential to plants?" did not appear until 1797. Other articles on the influence of oxygen on the germination of

seeds, the influence of soil on the constituents of plants, the potassium phosphate found in plants, etc., followed. In 1804, DE SAUSSURE assembled his various papers on plant chemistry and published them in book form under the title, "Recherches chimiques sur la Végétation". This small octavo volume of 327 pages, pronounced a classic by no less an authority than BERZELIUS, is a work that should be in the library of every agricultural chemist.

The scope of DE SAUSSURE's "Recherches chimiques sur la Végétation", a landmark in the history of crop chemistry and plant physiology, is indicated by the following translation of a part of the preface (pp. iv-viii).

"The functions of water and gases in the nutrition of plants and the atmospheric changes which they produce are the subjects which I have chiefly investigated. The observations of PRIESTLEY, of SENEBIER, and of INGEN-HOUZ opened the path which I have followed but they did not reach the objective which I had in mind. If the imagination filled at times the voids in their work it was with conjectures, whose obscurity and contradictions have always shown the uncertainty. I have employed in my proofs eudiometric methods using potassium hydrosulfide or phosphorus. These procedures have given my analyses an accuracy which was lacking in the nitrous gas method of eudiometry employed by my predecessors.

"My researches have enabled me to show that water and air contribute more to the formation of the dry substance of plants which grow upon a fertile soil than the humus matter which they absorb in aqueous solution through their roots.

"I have occupied myself also with another subject which has only given rise to hypotheses; it is that relating to the origin of the ash constituents of plants. I have sought by numerous experiments to determine the principles in accordance with which the ash constituents vary either in quantity or composition according to season, the nature of the plants and their different parts. This work has yielded me several new observations which prove that all the questions, just indicated, can be answered satisfactorily without attributing to plants creative forces and transmutations that contradict observed facts.

"In experiments upon plants so many different and unforeseen causes tend to influence the results that one should never refrain from indicating all the circumstances attending the investigations. The details into which I enter in this connection will serve to determine the degree of confidence that can be given to my results; they will help to prevent contradictions due to differences of method; they will help to explain errors from which I cannot flatter myself to have escaped in a series of long, difficult experiments which in their results are perhaps applicable only to the species of plants submitted to my examination. The task which I have prescribed is doubtless hard and wearisome but if one considers that the perfection of agriculture has been the object of my aim he will bear with its difficulties and be tolerant of its shortcomings."

The following abstracts of the different chapters give a brief synopsis of DE SAUSSURE's "Chemical Researches on Plants".

Chapter I. Influence of oxygen on germination (pp. 1-24). — Oxygen and water are two agents necessary for germination. Seeds do not germinate in an atmosphere of other gases (carbon dioxide, nitrogen, etc.). All seeds give off carbon dioxide during germination and the volume of this is very closely equal to the volume of oxygen absorbed. In putrefaction seeds give off carbon dioxide, carburetted hydrogen, and nitrogen. Seeds produce sugar during germination. The dry weight of seeds is less after germination, even when corrected for the carbon lost as carbon dioxide; the loss is explained by the formation and evolution of water from the substance of the seeds.

Chapter II. Influence of carbon dioxide on plants (pp. 25-59). — Carbon dioxide is the chief source of the carbon supply of plants but it is

useful to plants only in the quantities that they are able to assimilate; any excess beyond this is injurious. Plants die in gas mixtures that contain over fifty percent of carbon dioxide. Very small amounts of carbon dioxide are injurious if the assimilative process is checked by placing plants in darkness. If caustic lime is present to absorb the carbon dioxide the plants are not injured. Seven periwinkle plants were kept six days in an artificial atmosphere over mercury. The analysis of the air before and after the experiment was as follows (p. 42):—

	BEFORE EXPERIMENT	AFTER EXPERIMENT
	cc	cc
Nitrogen	4199	4338
Oxygen	1116	1408
Carbon dioxide	431	0
Total	5746	5746

The total volume of gases was the same before and after the experiment. The entire 431 cc of carbon dioxide was assimilated; 292 cc of oxygen and 139 cc of nitrogen were evolved.

Plants grown in distilled water in carbon dioxide-free air do not increase in carbon content. Mint plants containing 40.29 parts dry substance and 10.96 parts carbon, when grown in distilled water in open air and sunlight for two and a half months, yielded 62.00 parts dry substance and 15.78 parts carbon. The gain of 4.82 parts carbon was derived entirely from the carbon dioxide of the air. The same weight of mint plants in darkness lost carbon. While the green leaves are the assimilative organs of the vast majority of plants, the red or purple leaves of other varieties can also decompose carbon dioxide and liberate oxygen.

Chapter III. Influence of oxygen on grown plants (pp. 60–135).— The most noticeable effect of oxygen on vegetation is to produce carbon dioxide and in this form to give back to plants the elements which they can assimilate. The leaves of most green plants at night absorb oxygen and give off carbon dioxide, the latter, however, in less volume than the amount of oxygen consumed. Hence plants grown in a closed space diminish the volume of surrounding air at night but they increase it during the day by almost the same amount. The absorption of oxygen by plants is called inspiration and the liberation of carbon dioxide is called expiration. It is a true respiration process similar to that of animals. There is no inspiration if oxygen is not present. Inspiration is greater at 20–25°R. than at 10–15°R. Oxygen inspired by plants cannot be recovered by an air pump. Inspiration and expiration are as closely interrelated as the rise and fall of a pendulum. The assimilation process in sunlight by which carbon dioxide is absorbed and oxygen evolved must be carefully distinguished from the respiration process by which oxygen is absorbed and carbon dioxide evolved. Determinations of oxygen consumption by the leaves of 57 different species of plants kept 24 hours in darkness showed per unit volume of leaf an absorption of 8 volumes by beech leaves (*Fagus sylvatica*) and only 0.5 volume by lily leaves (*Lilium candidum*). The roots, wood, alburnum, petals, and other non-green parts of plants do not respire. A certain amount of oxygen, necessary for their vital functions,

is brought to them by the fluids of the plant and the carbon dioxide thus produced is transported in solution by the ducts of the plant to the leaves

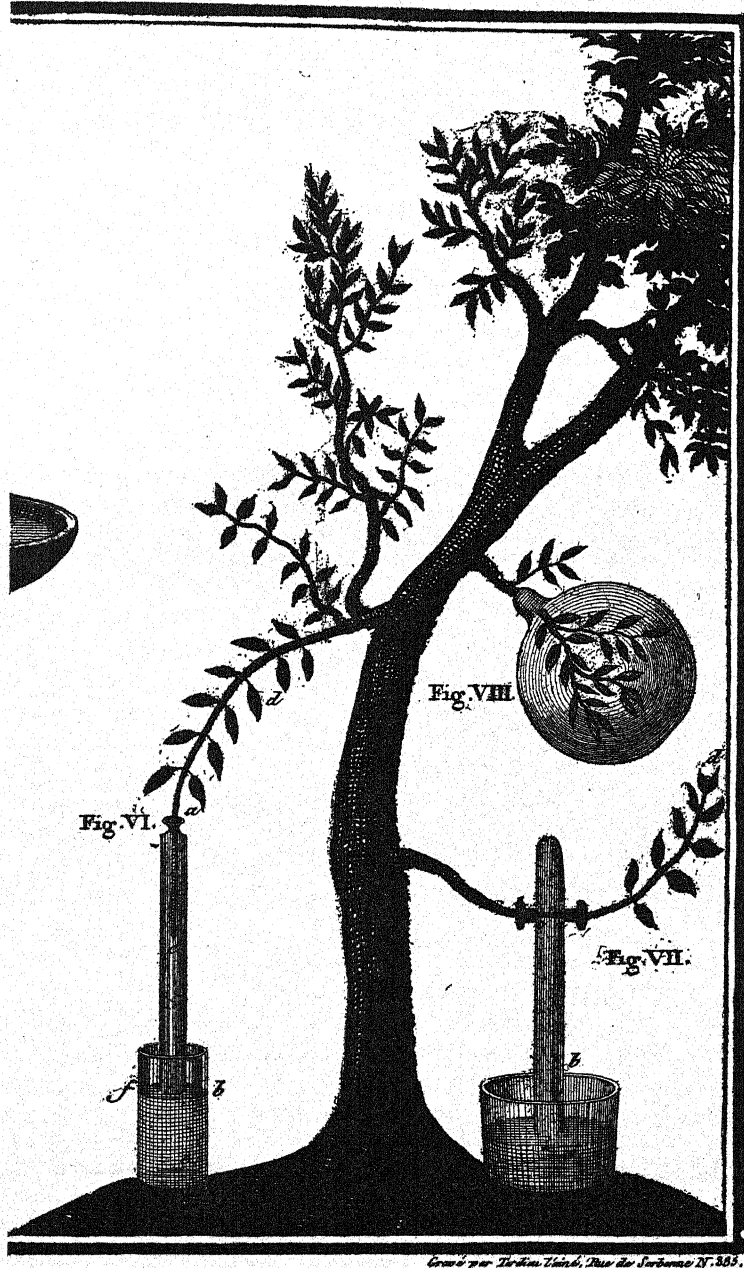


FIG. 28. — Apparatus of DE SAUSSURE to determine the changes effected in the composition of an enclosed volume of air by leaves (Fig. VIII), by a twig stripped of its leaves (Fig. VI) and by the leafless part of a branch (Fig. VII).

where it is decomposed, the carbon being fixed and the oxygen again liberated.

Chapter IV. Influence of oxygen on certain proximate constituents of plants (pp. 136-161). — This chapter relates to the rôle of oxygen in the precipitation of vegetable extracts, in acetification, in the decay of wood, in putrefaction and in the oxidation of turpentine and linseed oil. DE SAUSSURE concludes from his experiments that

"in general (with the exception of oils) oxygen, in the first stages of fermentation, is not fixed in the dead plant materials, does not unite with their hydrogen to form water and only acts by removing part of their carbon. Thus in acetification, in the precipitation of extracts, and in the coagulation of vegetable albumen, oxygen is used only for the withdrawal of this carbon. The proportion of carbon, however, in the combined residue after this withdrawal is not diminished, for the plant substances involved liberate at the same time a part of their oxygen and hydrogen in the form of water.

"But oxygen does unite either with the hydrogen of the dead plant materials, or with their whole substance, when they begin to putrefy or at that point of their fermentation when they can liberate hydrogen. Since the time of this combination coincides with that when hydrogen is liberated, since also the latter is no longer found in the gaseous oxygen with which the putrefying plant is in contact and since finally the production of water is greatly increased at this stage of fermentation it is natural to suppose that the oxygen, which has disappeared and does not occur in the carbonic acid gas produced at the same time, is not assimilated by the plant substance but is used to form water.

"There is an important difference in the fermentation products obtained when oxygen is absent and when it is present. In the first case the carbonic acid gas which is liberated obtains its two elements in the fermenting plant material, while in the second case, the acid gas seems to draw only one of its elements (carbon) from the fermenting substance" (pp. 159-61).

In an experiment with turpentine DE SAUSSURE found that it absorbed in four months twenty times its volume of oxygen and liberated only one quarter of this volume in carbon dioxide. An experiment with linseed oil indicated an absorption in four months of twelve times its volume of oxygen without liberating a noticeable amount of carbon dioxide. It was the only plant or animal substance in DE SAUSSURE's experience that exhibited this behavior.

Chapter IV is the least satisfactory part of DE SAUSSURE's book. He recognized different types of fermentation but his explanations and conclusions are exceedingly faulty. He touched upon problems that puzzled LIEBIG and other later investigators and some of them were not successfully solved until after the time of PASTEUR.

Chapter V. Vegetable Humus (pp. 162-93). — Humus is defined as the black substance into which dead plants are resolved on exposure to the combined action of oxygen and water. The carbon content of humus is greater than that of the original plant materials which produce it. Destructive distillation of 10.614 grams each of dry oak wood and of dry oak wood humus yielded the following products (p. 164).

OAK WOOD				OAK WOOD HUMUS			
Carburetted hydrogen	..cc.	2293				2456	
Carbon dioxidecc.	575				673	
Watergrams	4.25	{ contained ammonium pyrolignite with excess of pyroligneous acid			2.81	{ contained ammonium pyrolignite and am- monium carbonate
Empyreumatic bituminous oil		0.589				0.530	
Residual carbon	2.23	(contained .026 gm ash)			3.13	(contained 0.424 gm ash)

So far as these results permit one to judge, the humus shows an enrichment in carbon and mineral matter and a diminution in hydrogen and oxygen, as compared with the original wood. On continuous exposure to air and rain humus continues to lose in weight but without much change in its percentage of carbon, hydrogen, and oxygen, the latter two elements being split off in the right amounts as water while the carbon is being evolved as carbon dioxide. A small amount of humus is also being continually dissolved by the soil drainage water. The solubility of humus in water is slight, 10,000 parts of distilled water after five days contact yielding only 26 parts of dry extract. Twelve successive extractions with boiling water dissolved 11 percent of the weight of humus. The weight of a crop grown on extracted humus was one quarter less than that obtained on the original unextracted humus. After 50 extractions humus still continued to give a small amount of extract. On exposing to the air for 3 months this quantity was increased. Acids dissolve but little of the organic matter of humus but potash and soda dissolve it almost completely. Humus when exposed with water does not ferment. It has in fact an antiseptic action and checks the fermentation and putrefaction of plant and animal substances. Humus on incineration gives several percent of ash which, because of its vitreous condition, is not easily soluble in water. The aqueous extract of humus, however, gives an ash which yields a considerable amount of potash, muriates and sulfates of the alkalis and other water soluble salts. DE SAUSSURE concludes that humus extract has a certain amount of fertilizing action and that its ash contains all the principles of plant ashes.

Chapter VI. Growth of plants in oxygen-free atmospheres (pp. 194–216).—Plants that have a sufficient area of green leafy tissue can survive in an atmosphere of nitrogen and hydrogen owing to their ability to produce free oxygen from the carbon dioxide in the tissues of the plant. If there is no exterior source of carbon dioxide a condition of maintenance without growth is then reached, the plant evolving by day the amount of oxygen it consumed at night and evolving at night the amount of carbon dioxide it assimilated by day. The oxygen need of the plant for maintenance is small.

An excess of carbon dioxide is much more injurious to plants in an atmosphere of nitrogen than in one of common air. Carbon dioxide is always harmful when it is present beyond the assimilative power of the plant. Oxygen appears to stimulate assimilation. Plants do not assimilate gaseous nitrogen; for their supply of this element they are dependent upon decomposing plant and animal remains and upon the ammonia of the air. Plants do not assimilate hydrogen, although an atmosphere of this gas is diminished slightly, owing to its decomposing the carbon dioxide evolved by the plant with production of water and carbon monoxide. This statement of DE SAUSSURE is of interest as a possible explanation of the presence of carbon monoxide in the gases from submerged soils. ROBINSON (*Soil Science* 30: 209) found carbon monoxide in such gases to be always associated with a considerable amount of hydrogen; when hydrogen was lacking there was no carbon monoxide.

Certain green plants appear to survive in a vacuum, if direct sunlight

be avoided, owing to their ability to produce free oxygen. Seeds germinate in a vacuum very incompletely. Slight evidences of growth may be due to traces of oxygen not removed by the air pump.

Chapter VII. Fixation and decomposition of water by plants (pp. 217–39). — Plants assimilate the oxygen and hydrogen of water to form part of their solid substance, but only when carbon is assimilated at the same time. When plant tissues that have assimilated the oxygen and hydrogen of water ferment in absence of oxygen, they produce carbonic acid by the decomposition of their own substance. The oxygen of the assimilated water unites with the carbon of the plant to form this gas and the living green parts of plants, when they assimilate this carbon dioxide, liberate indirectly the oxygen that had previously belonged to the water. But plants in no case liberate oxygen directly by the decomposition of water and assimilation of its hydrogen. The oxygen must first combine with carbon to form carbon dioxide.

Some plants with thick leaves (as cactus), when growing in air deprived of carbon dioxide, liberate several times their volume of oxygen. But this gas, although it belonged originally to water, is formed only in the sunlight by the decomposition of the carbon dioxide which they form entirely from their own substance. If the evolved carbon dioxide is absorbed by caustic alkali, suspended near the plant, no free oxygen is produced. The exclusive property which thick-leaved plants have of forming carbon dioxide from their own substance is due to the slight porosity of their epidermis or to the slight contact which their interior parts have with the outside oxygen.

The apparent exception in the case of thick-leaved plants to the statement of SENEBIER (1788) that carbon dioxide is an absolute essential to the evolution of oxygen by green plants was thus explained by DE SAUSSURE in 1804. The subject was not referred to again until over 70 years later when ADOLF MAYER (1875) made the same observation in the case of fleshy plants of the houseleek family (*Crassulaceae*). He noted that simultaneously with the evolution of oxygen in the sunlight there was a decrease in the acid content of the leaves. The organic acids of green leaves would thus appear to be decomposed by sunlight into oxygen, and this MAYER regarded as an exception to SENEBIER's rule. DE VRIES (1884), however, attributes the disappearance of the organic acids in the leaves of fleshy plants not to the action of sunlight on chlorophyll tissue, but to an oxidation process which converts the acids into water and carbon dioxide. The latter, formed within the plant, is then decomposed in sunlight by photosynthesis with liberation of oxygen. The rule of SENEBIER and the explanation of DE SAUSSURE are thus vindicated.

Chapter VIII. Absorption of solutions by the roots of plants (pp. 240–72). — Most careful investigations were made by DE SAUSSURE upon the mineral constituents of plants. In commenting upon the theory held by VAN HELMONT and many subsequent writers that plants could synthesize their ash components, DE SAUSSURE made the following pertinent remark (p. 242) :—

"These authors have supposed that the vital force, whether animal or vegetable, could, by decomposing, or combining in different ways, the atmospheric air and water

produce all substances, even the salts, earths and metals which analysis and incineration detect in plants. This confused idea is no more susceptible of proof than that of making gold out of substances which do not contain it. Before having recourse to unintelligible miraculous transmutations which contradict all observed facts, it is necessary to be absolutely certain that plants do not find these principles already existing in the environment where they develop."

The views of other writers that plants derive their mineral and nitrogenous matter from the air and that fertilizers owe their nutritive action to the gases which they develop are also contradicted by DE SAUSSURE (pp. 246-7) :—

"If fertilizers promote vegetable growths chiefly by the gases that they develop, a fallow field which produces no crop should be exhausted as much as the one that bears a rich harvest. All the operations of agriculture, however, prove the exact contrary. Cropping impoverishes the soil and it produces this effect more or less according to the nature of the crop. In general annual plants, rich in vegetable matter and with abundant transpiration, exhaust the soil more than evergreens, whose growth is less rapid, and than annual plants with succulent leaves and low transpiration, such as peas, beans, and buckwheat. A corollary of the preceding observation, which can serve as another proof, is that, other things being equal, the most exhausting crops require a soil that is richest in nutrients."

The roots of plants have a selective power and do not assimilate mineral constituents in the same proportion in which they occur in the soil solution. DE SAUSSURE prepared 10 solutions containing 0.637 g. each of potassium chloride, sodium chloride, calcium nitrate, sodium sulfate, ammonium chloride, calcium acetate, copper sulfate, crystallized sugar, gum arabic, and 0.159 g. of humus extract (calculated as dry substance) in 793 cc of solution. Plants of lady's thumb (*Polygonum persicaria*) grown 5 weeks in the shade in these solutions, when their volumes had diminished one half, showed the following percentage absorption (p. 251) :—

INGREDIENT	PERCENTAGE ABSORBED	REMARKS
Copper sulfate	47	Plants lived only two to three days.
Sugar	29	Plants could exist only by replacing fermented with fresh solutions.
Potassium chloride	14.7	Plants grew and developed roots.
Sodium sulfate	14.4	Plants grew and developed roots.
Sodium chloride	13	Plants grew and developed roots.
Ammonium chloride	12	Plants failed to grow and were sickly.
Gum	9	Plants died in eight to ten days.
Calcium acetate	8	Plants died in eight to ten days.
Extract of humus	5	Plants grew and developed roots.
Calcium nitrate	4	Plants grew and developed roots.

The experiment showed that water was assimilated much faster than its dissolved substances. The high absorption of copper sulfate was evidently due to killing of the roots when their selective power was destroyed. Removal of roots in fact destroyed all power of selection and dissolved substances were absorbed almost in the same proportion as in the solution. Variations in assimilation were also noted with solutions that contained several substances. DE SAUSSURE attributed these variations in large part to differences in viscosity. Water, the most fluid of the substances is

absorbed in greatest amount, while gum which gives a very viscous solution is assimilated to a much less extent than sugar.

DE SAUSSURE opposed the view, held by many, that the mineral ingredients of plants, because of their relatively small amounts, were unessential. This might be true of certain elements that are assimilated but it has not been demonstrated for those that are always present. Small quantity is not an index of lack of utility. Different crops vary in their requirements. Calcium sulfate promotes the growth of lucerne, clover, and sanfoin; on other crops it has no effect. The dissolved humus, salts and other constituents of the soil solution which are assimilated by the roots of green plants constitute only a very small part of their substance. Their quantity, though small, has nevertheless a very powerful influence on the growth of plants, the greater part of whose substance, however, is derived from water and carbon dioxide.

Chapter IX. Observations on the ashes of plants (pp. 272-327). — DE SAUSSURE's twenty-seven tables of analyses giving the percentages of water-soluble salts, insoluble phosphates and carbonates, silica, alumina, and metallic oxides in the ashes of the leaves, branches, wood, bark, flowers, and fruit of seven different trees, in the ashes of the straw and grain of wheat, maize, barley, and oats, and in the ashes of the organs of various shrubs, are classic as they constitute the first tabulations of the kind. Although highly imperfect in the light of present knowledge they mark the initiation of an important new development in the history of agricultural chemistry. A few of his results are tabulated herewith: —

PERCENTAGE AND COMPOSITION OF ASH OF SEVERAL CROPS: —
(Tables des Incinérations et des Analyses, T. DE SAUSSURE, 1804)

	Beans		Wheat		Maize	
<i>Type of Soil</i>	Garden, clayey		Fertile, gravelly		Garden, clayey	
<i>State of Crop</i>	Mature		Mature		Mature	
<i>Time of Harvest</i>	July 23		July 28, 1803		July 23, 1803	
	Whole plant	Grain	Straw	Grain	Stalks	Grain
<i>Ash, percent in dry sub.</i>	11.5	3.3	4.3	1.3	8.4	1.0
Percentage Composition of Ash						
<i>Potash</i>	31.	22.45	12.5	15.	59.	14.
<i>Phosphate of Potash</i>		43.93	5.	32.	9.7	47.5
<i>Muriate of Potash</i>	14.	0.9	3.	0.16	2.5	0.25
<i>Sulfate of Potash</i>	2.	2.	2.	trace	1.25	0.25
<i>Earthy Phosphates</i> ..	6.	27.92	6.2	44.5	5.	36.
<i>Earthy Carbonates</i> ..	37.5	0.	1.	0.	1.	0.
<i>Silica</i>	2.75	0.	61.5	0.5	18.	1.
<i>Metallic Oxides</i>	0.75	0.50	1.0	0.25	0.5	0.12
<i>Loss</i>	6.	2.30	7.8	7.59	3.05	0.88
Total	100.	100.	100.	100.	100.	100.

The results show that the percentages of ash are several times greater in the straws than in the respective grains of the three crops, that the

percentages of silica are much higher in the ashes of the straws and that the percentages of phosphates are much higher in the ashes of the grains.

While the losses and undetermined matter in DE SAUSSURE'S tabulations indicate the desirability of greater improvements in analytical methods, his determinations are a great advance over previous work in this field. DE SAUSSURE by his tabulations of species of plant, plant product, character of soil on which the plant was grown, percentage of plant ash and percentage of composition of such ash, was able to establish correlations that afterwards became fundamental laws of our present science of agricultural chemistry. His method is the only one that enables the investigator to determine the specific influence of any single factor upon the growth of a crop among a large number of disturbing variables.

Here as in other chapters of his book DE SAUSSURE is cautious about making sweeping generalizations.

"In a subject as new and as complicated as this one the explanations that I give are doubtless very often venturesome, but I have grounds for believing that the observations on which they are based are correct at least for the species of plants that I have examined. Although many incinerations were made they are perhaps not always sufficient to conduct us to general conclusions" (pp. 274-5).

In his critical review of previous work upon plant ash DE SAUSSURE explains the reasons of many discrepancies, such as neglect to take account of the moisture content of the material. His own analyses were made upon the same weights of dry substance. With regard to the general composition of plant ashes DE SAUSSURE remarks:—

"Salts of the alkalis potash and soda; phosphates of the earths lime and magnesia; lime free or as carbonate; silica and the oxides of iron and manganese, either separate or combined, form the chief constituents of plant ashes and the only ones that have occupied my attention; they may contain many others which because of their small quantity very often escape our notice. The ashes perhaps contain all known substances that resist volatilization by the fire employed for combustion. It is possible that our atmosphere holds all elements in suspension and that an exhaustive analysis would show traces of them in all soils" (p. 280).

A few of the more general of DE SAUSSURE'S conclusions relating to the ashes of plants are the following:

The different organs of plants vary in the content and composition of their mineral matter. Mineral constituents are more abundant where transpiration is most active; the leaves of plants yield more ash than the fruit, the bark more ash than the wood. Owing to their greater transpiration the leaves of deciduous trees yield more ash than leaves of evergreens.

The total mineral content of herbaceous plants reaches its maximum before the flowering stage and thereafter begins to decline. This is due to the gradual dying of leaves and the loss of their ash ingredients by the leaching action of rain. As plant tissues become dead or inactive a part of their mineral matter passes to the vegetating organs.

The dry substance of a decayed plant, that has not been exposed to excessive leaching, yields more ash than that of a sound plant of the same variety.

The nature of the soil has a pronounced influence upon the mineral constituents of plants, the proportion of elements in the latter being re-

lated to that in the soils; thus plants growing on a soil of silicious origin contain more silica and less lime than the same variety of plants growing on a calcareous soil. The view of LAMPADIUS and others that silica is produced by the vital processes of the plant has no scientific support.

Plants of different varieties growing on the same soil differ in the content and composition of their mineral matter owing to differences in assimilative power and not to a special vital creative process as some authorities continue to maintain.

Because of the minute descriptions of the methods of analysis which he employed DE SAUSSURE might be regarded as the founder of agricultural chemical analysis. The methods for the determination of carbon and of mineral constituents, described in his treatise of the year 1804, were however imperfect and represent the art only in its infancy. He was a careful experimenter and extremely conscientious in the statement of his results. His book is the first important work to employ the metric system which was introduced in 1801.

DE SAUSSURE continued his researches, in agricultural chemistry and in the improvement of analytical methods, for nearly forty years after the publication of his book. He was the first to make an accurate combustion analysis of alcohol, as is shown by the following table: —

	CARBON PERCENT	HYDROGEN PERCENT	OXYGEN PERCENT
LAVOISIER	29.0	16.6	54.4
DE SAUSSURE	52.0	13.7	34.3
Theoretical	52.2	13.0	34.8

Subsequent publications by DE SAUSSURE, on the conversion of starch into sugar, alterations of vegetable substances by boiling, variations in the carbonic acid content of the air in winter and summer, decomposition of starch at atmospheric temperature by air and water, influence of green fruits on air, formation of sugar in the germination of wheat, alteration of air in germination and fermentation, and other agricultural chemical subjects, were published in the "Annales de Chimie", the "Bibliothèque universelle", and other scientific journals.

Of these later publications reference will be made only to one of his final papers "On the Nutrition of Plants", of which a German translation was published in LIEBIG's Annalen for 1842 (Vol. 42, pp. 275-91). In this paper DE SAUSSURE, on the basis of water culture experiments, stated that a dark brown solution of potassium humate promoted the growth of beans and lady's thumb (*Polygonum persicaria*) with absorption by these plants of some colored humate from solution. While recognizing the dominant rôle which assimilation of atmospheric carbon dioxide plays in the growth of plants, DE SAUSSURE held that soil humus, especially when it had been brought into solution by alkalies and by fermentation, was an important aid in plant nutrition. The fertilizing action of dung liquor he attributed not only to the plant nutrients which it contained but to its fermentative action in hastening the decomposition and solution of the insoluble organic matter of the soil. In this connection he remarked: —

"When LIEBIG asserts that the nutrition of plants in the most fertile soil takes place only through the decomposition of carbon dioxide, the union of the elements of water

and the absorption of salts, he bases his theory on the unavailability of the soluble organic matters which occur in the soil where the plants are grown. Before we investigate the facts which he cites in this connection, we must recognize that plants can increase their organic substance without other nutrients than water and atmospheric air. We will find, however, at the same time, that the plants produced by this kind of nutriment have almost no value in agriculture" (*loc. cit.*, p. 288).

As a general summary of his experiments DE SAUSSURE concluded: —

(1) "That fertile soil contains a mixture of soluble and insoluble organic substances and that the entrance of the former into plants through the roots is a most important aid for the nourishment which they derive from air and water.

(2) "That the insoluble organic substances, which occur in the soil in much greater amount than the preceding, undergo with the aid of water a slow fermentation which produces therefrom a nutritive soluble substance that can partially and gradually replace the former.

(3) "That plants obtain their nitrogen almost wholly by absorption of the soluble organic substances: direct experiment shows that they do not assimilate it to an appreciable extent in the gaseous condition and that it does not occur as ammonia in the water supplied for absorption.

(4) "That a difference exists between the colored substances that can serve as plant nutrients and those that lack this property. That the former on absorption change their color and unite with the plant, while the latter, in case they enter the plant, undergo no change.

"Since the colored extractive substances, that serve as plant nutrients, are absorbed by the plants and are not found again unchanged either in the residue after absorption, or in the secretions of the plant, or in their atmosphere, or in the plant itself, we must conclude that they have disappeared through the assimilation of a part of their elements by the plant" (*loc. cit.*, pp. 289-90).

DE SAUSSURE with some qualifications thus entered the lists with THAER, DAVY, DE CANDOLLE, BERZELIUS and other defenders of the humus theory of plant nutrition. These men, whose births all fell between 1750 and 1780 were no doubt too firmly grounded in the traditions of their time to adopt so radical a doctrine as the complete rejection of the age-long humus theory of plant nutrition. DE SAUSSURE's respect for the observations of his father on vegetable humus (*Recherches chimiques*, pp. 177-79) no doubt also played some part in his defense of this theory.

LIEBIG (1842) followed DE SAUSSURE's article in the *Annalen* with a six-page criticism in which he held that the growth of the latter's experimental plants was due to the assimilation of the mineral constituents of the humus and not of its organic matter; and furthermore that, even if humus was assimilated, its amount was so trivial in comparison with the great gains in weight made by the plants that it could play no significant rôle as a plant nutrient. Further developments in the humus controversy are discussed in the following chapter under the accounts of the works of SPRENGEL, of MULDER, and of LIEBIG.

DE SAUSSURE had the satisfaction of living long enough to witness the rich fruitage of his early "*Recherches chimiques sur la Végétation*" in the great influence which it exercised on later agricultural chemical developments. His life was uneventful and his habits were those of a recluse. He served, however, at various times as a member of the Council of the Republic of Geneva and was president of the Scientific Congress at Lyon in 1841. He had a fondness for literature and was a conservative in politics. He died at Geneva on April 18, 1845.

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Humphry Davy (1778-1829):— The first eminent chemist that used the title "Agricultural Chemistry" for a treatise upon the subject was Sir HUMPHRY DAVY. He made, however, few important additions to this branch of chemical science and his greatness as a chemist depends upon discoveries made in other fields.

DAVY was born at Penzance, England, and attended school here and at Truro. After the death of his father, he was apprenticed to an apothecary, in whose place his first interest in chemistry was aroused. He read the treatise of LAVOISIER and conducted experiments with such meager equipment as could be found. When Dr. BEDDOES established his Medical Pneumatic Institution at Bristol, he made DAVY its superintendent. In his study of the physiological effects of different gases DAVY discovered in 1799 the peculiar intoxicating property of nitrous oxide, a discovery that greatly enhanced his reputation. In 1801 Count RUMFORD appointed him lecturer and in 1802 professor at his recently established Royal Institution of London. It was here that DAVY made his greatest discoveries. By means of the electric current he isolated the elements potassium and sodium in 1807 and the elements barium, strontium, calcium, and magnesium in 1808. In 1810 he demonstrated that SCHEELÉ's dephlogisticated muriatic acid gas (afterwards called oxymuriatic acid) was not a compound but an element which he named chlorine. His invention of the safety lamp in 1816 greatly helped to remove the dangers of gas explosions in coal mines. He declined to patent the idea but dedicated it to the "cause of humanity" about which he was always solicitous. In 1827 DAVY suffered a stroke of paralysis; other attacks succeeded and he finally died at Geneva on May 29, 1829, at the early age of fifty-one.

DAVY'S book on agricultural chemistry was the outgrowth of a course of memorable lectures which he was asked to deliver before the British Board of Agriculture in 1802. These lectures were continued until 1812, when they were assembled and published in 1813 under the title, "Elements of Agricultural Chemistry". It is to the first London edition of this work that the following citations refer.

It is desirable first to ascertain what DAVY means by "Agricultural Chemistry". He speaks as follows in his introductory lecture:—

"Agricultural Chemistry has not yet received a regular and systematic form. It has been pursued by competent experimenters for a short time only; the doctrines have not as yet been collected into any elementary treatise; and on an occasion when I am obliged to trust so much to my own arrangements, and to my own limited information, I cannot but feel diffident as to the interest that may be excited, and doubtful of the success of the undertaking. I know, however, that your candour will induce you not to expect any thing like a finished work upon a science as yet in its infancy; and I am sure you will receive with indulgence the first attempt made to illustrate it, in a distinct course of public lectures.

"Agricultural Chemistry has for its objects all those changes in the arrangements of matter connected with the growth and nourishment of plants; the comparative values of their produce as food; the constitution of soils; the manner in which lands are enriched by manure, or rendered fertile by the different processes of cultivation. Enquiries of such a nature cannot but be interesting and important, both to the theoretical agriculturist, and to the practical farmer. To the first they are necessary in supplying most of the fundamental principles on which the theory of the art depends. To the second, they are useful in affording simple and easy experiments for directing his labours, and for enabling him to pursue a certain and systematic plan of improvement.

"It is scarcely possible to enter upon any investigation in agriculture without finding it connected, more or less, with doctrines or elucidations derived from chemistry" (pp. 3-4).

It will be noted that DAVY speaks of agricultural chemistry as "a science as yet in its infancy" so that the question "Is Agricultural Chemistry a Science?" is answered at once by him in the affirmative. His definition of this science in the light of later developments is somewhat restricted for he limits its scope to (1) the constitution of soils; (2) their improvement by manure and cultivation; (3) the growth and nourishment of crops; and (4) the comparative values of crop produce as food. DAVY's "Agricultural Chemistry" is in part a compilation of the work of previous writers and he quotes freely from the publications of HERMBSTÄDT, EINHOF, DE SAUSSURE, GAY-LUSSAC and THENARD, and other investigators, some of whose tables of results are employed in his development of the subject. The book is noteworthy for its list of 47 chemical elements with descriptions of properties and combining powers so far as determined. It is the most complete list that had yet appeared. Among the elements named are sodium, potassium, calcium, strontium, barium, and magnesium which DAVY was the first to isolate. Oxymuriatic acid, which DAVY proved to be an element and renamed chlorine, appears for the first time under this new designation. DAVY was among the first to call attention to the fact that the number of chemical elements, with which agricultural chemistry is concerned, is limited.

"For pursuing such experiments on the composition of bodies as are connected with agricultural chemistry, a few only of the undecompounded substances are necessary; and amongst the compounded bodies, the common acids, the alkalies, and the earths, are the most essential substances. The elements found in vegetables, as has been stated in the introductory lecture, are very few. Oxygene, hydrogene, and carbon constitute the greatest part of their organized matter. Azote, phosphorus, sulphur, manganese, iron, silicum, calcium, aluminum, and magnesium, likewise, in different arrangements, enter into their composition, or are found in the agents to which they are exposed; and these twelve undecompounded substances are the elements, the study of which is of the most importance to the agricultural chemist" (p. 47).

DAVY stresses the importance of chemical analysis in the following words: —

"All the different parts of plants are capable of being decomposed into a few elements. Their uses as food, or for the purposes of the arts, depend upon compound arrangements of those elements which are capable of being produced either from their organized parts, or from the juices they contain; and the examination of the nature of these substances is an essential part of Agricultural Chemistry" (p. 64).

DAVY names 19 classes of the compound substances found in plants (p. 65): (1) gum, or mucilage and its different modifications; (2) starch; (3) sugar; (4) albumen; (5) gluten; (6) gum elastic; (7) extract; (8) tannin; (9) indigo; (10) narcotic principle; (11) bitter principle; (12) wax; (13) resins; (14) camphor; (15) fixed oils; (16) volatile oils; (17) woody fibre; (18) acids; (19) alkalies, earths, metallic oxides and saline compounds. The properties and elementary composition of each of these are given so far as available data permitted. The classification is obviously only a very rough one and is illustrative of the undeveloped state of chemistry at that time. Accurate physical and chemical methods for the identification of plant substances had not yet been sufficiently elaborated. In this connection DAVY remarks: —

"If slight differences in chemical and physical properties be considered as sufficient to establish a difference in the species of vegetable substances, the catalogue of them might be enlarged to almost any extent. No two compounds procured from different vegetables are precisely alike; and there are even differences in the qualities of the same compound, according to the time in which it has been collected, and the manner in which it has been prepared" (p. 105).

DAVY describes methods for the proximate and elementary analysis of plant products. He quotes EINHOF's analyses of potatoes, barley, rye, beans, etc. and gives a table of his own analyses of 37 different grains, vegetables, root crops, and grasses with their content of soluble or nutritive matter, mucilage or starch, saccharine matter or sugar, gluten or albumen, and extract, or matter rendered insoluble during evaporation (p. 131). The comparative values of crop produce for feeding purposes are developed principally by DAVY in an appendix of 63 pages in which he discusses the food value of 97 different grasses according to experiments conducted on the estate of the Duke of Bedford. The nutritive values were calculated from the weight of water-soluble matter, the grasses containing the highest amount of water-soluble constituents being regarded as the most nutritious. DAVY considered this method, which would now be regarded as highly imperfect, "sufficiently accurate for all the purposes of agricultural investigation". Methods of determining the nutritive value of feed stuffs by digestion experiments upon farm animals were not introduced until many decades later.

In his lecture upon the composition of the atmosphere and its influence upon vegetation DAVY confirms the basic experiments of PRIESTLEY, INGEN-HOUSZ, SENEBIER, and DE SAUSSURE upon the photosynthetic process by which carbon dioxide is assimilated from the air and oxygen evolved. The reverse, or respiration, process by which oxygen is absorbed and carbon dioxide eliminated, as in the germination of seeds, is also fully described. With regard to the origin of the nitrogen, or azote, of plants DAVY is non-committal. He only states: —

"When glutenous and albuminous substances exist in plants, the azote they contain may be suspected to be derived from the atmosphere: but no experiments have been made which prove this; they might easily be instituted upon mushrooms and funguses" (p. 203).

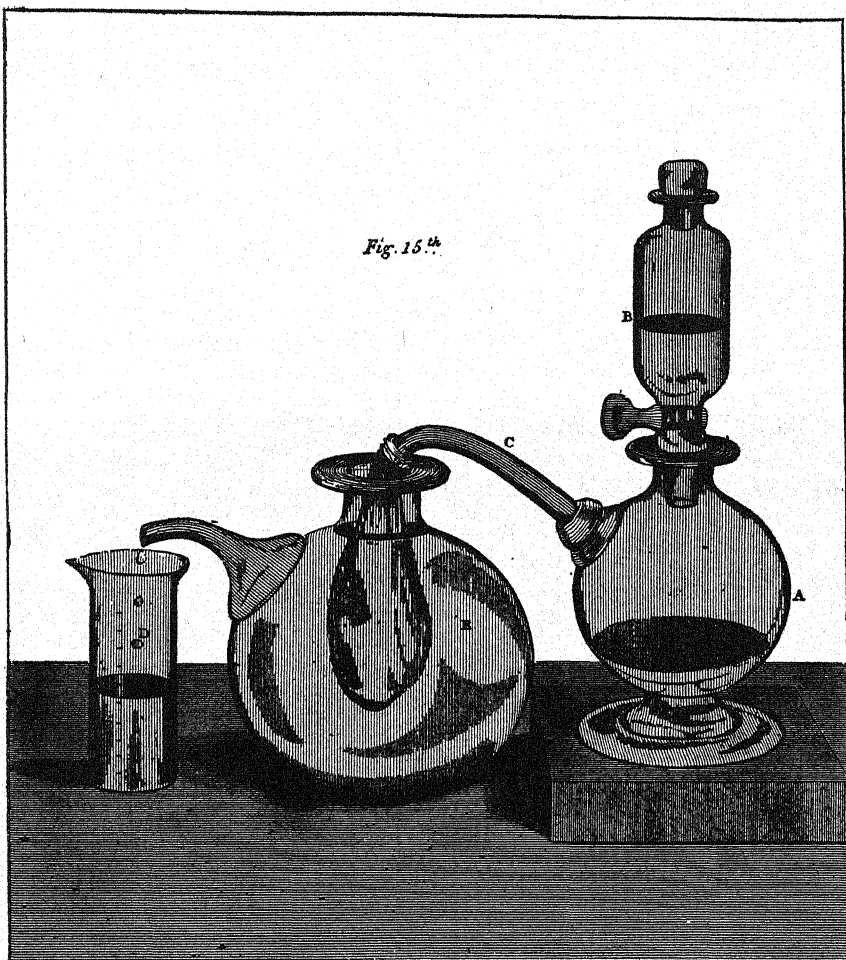


FIG. 29.—*Davy's Apparatus for Determining Carbon Dioxide in Soils.*—A weighed amount of soil is placed in the globular vessel A, into the neck of which fits the container B. The tube C connects A with a bladder immersed in water filling the vessel E. A graduated cylinder D is placed under the overflow tube of E. When hydrochloric acid is admitted from B into A, the evolved carbon dioxide distends the bladder and forces a corresponding volume of water into D. Illustration from DAVY's "Elements of Agricultural Chemistry", First Edition, London, 1813.

The problem of the origin of the nitrogen in plants, which was so actively debated a few decades later, was not fully cleared up until over a half-century after DAVY's time.

The obscure chemical processes, which take place within the plant, are indicated by DAVY only in rough outline:—

"When the similarity of the elements of different vegetable products is considered . . . it is easy to conceive how the different organized parts may be formed from the same sap, according to the manner in which it is acted on by heat, light, and air. By the abstraction of oxygene, the different inflammable products, fixed and volatile oils, resins, camphor, woody fibre, &c. may be produced from saccharine or mucilaginous fluids; and by the abstraction of carbon and hydrogen, starch, sugar, the different vegetable acids and substances soluble in water, may be formed from highly combustible and insoluble substances. Even the limpid volatile oils which convey the fragrance of the flower, consist of different proportions of the same essential elements, as the dense woody fibre; and both are formed by different changes in the same organs, from the same materials, and at the same time" (p. 206).

The movement of sap in plants, the formation of woody tissue, the effects of grafting, and the protection of plants against canker, mildew, insects and other pests are among the other subjects treated by DAVY in his interesting discursive style.

In discussing the chemical composition of soils DAVY mentions silica, lime, alumina, magnesia, oxides of iron and manganese, vegetable and animal matter and soluble saline compounds as the chief constituents. He devotes over 20 pages to methods for analyzing soils and describes a calimeter of his own invention for estimating their lime content.

A list of the leading mineral constituents of soil is given and the chief geological formations of Great Britain and Ireland are described. In discussing the physical properties of soils DAVY emphasizes the importance of water-holding capacity.

"Water, and the decomposing animal and vegetable matter existing in the soil, constitute the true nourishment of plants; and as the earthy parts of the soil are useful in retaining water, so as to supply it in the proper proportions to the roots of the vegetables, so they are likewise efficacious in producing the proper distribution of the animal or vegetable matter; when equally mixed with it they prevent it from decomposing too rapidly; and by their means the soluble parts are supplied in proper proportions" (p. 161).

In his lecture upon fertilizers DAVY discusses the various manures of vegetable origin (green manures, oil seed cakes, sea weed, straw, peat, wood ashes) and numerous animal products (fish, bones, horn, hair, blood, tanners refuse, coral, dung, urine, guano, etc.). DAVY was an advocate of the so-called "humus" theory of plant nutrition, which was also supported by THAER and other writers of this period. He states: —

"The great object in the application of manure should be to make it afford as much soluble matter as possible to the roots of the plant; and that in a slow and gradual manner, so that it may be entirely consumed in forming the sap or organized parts of the plant.

"Mucilaginous, gelatinous, saccharine, oily, and extractive fluids, and solution of carbonic acid in water, are substances that in their unchanged states contain almost all the principles necessary for the life of plants; but there are few cases in which they can be applied as manures in their pure forms; and vegetable manures, in general, contain a great excess of fibrous and insoluble matter, which must undergo chemical changes before they can become the food of plants" (p. 237).

Fermentation (as in the composting of straw with animal excreta) and atmospheric oxidation are the chief agencies, according to DAVY, by which the insoluble organic constituents of manure are dissolved and made available as plant food. Excessive fermentation, which is akin to combustion,

Fig. 17.

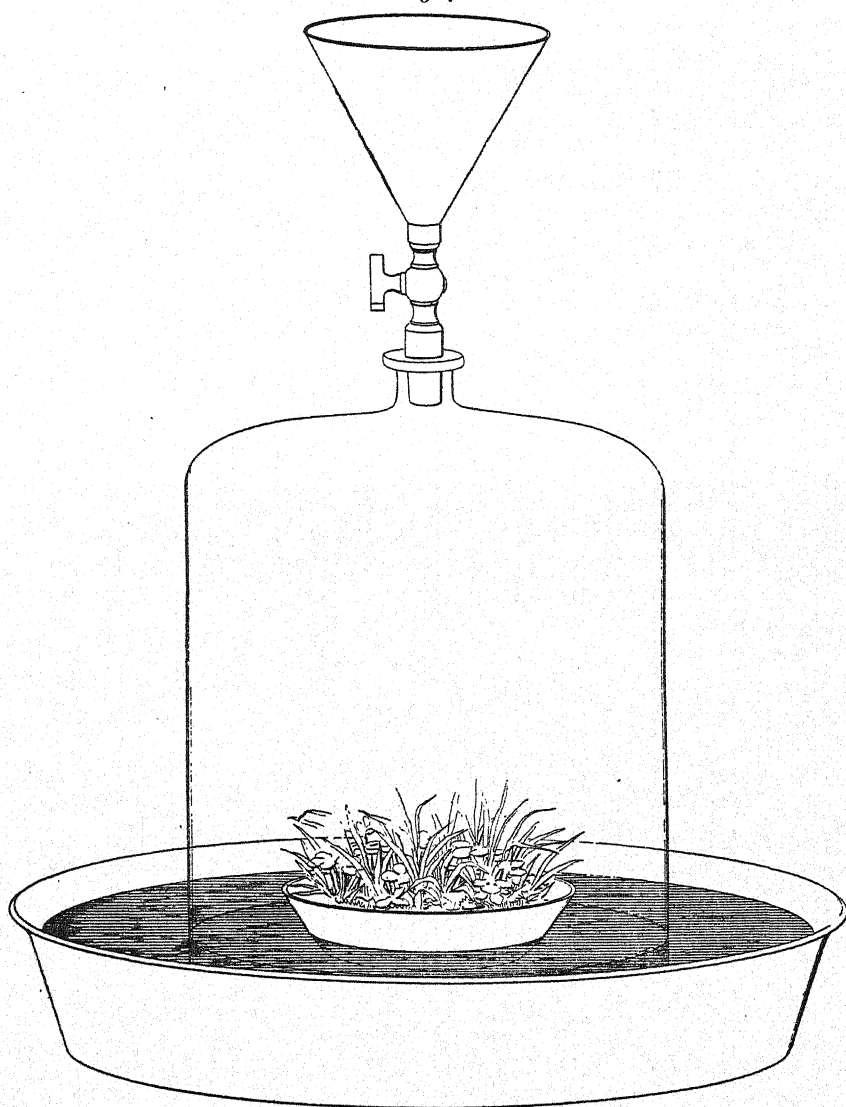


FIG. 30. — *Davy's Apparatus for Studying the Gases Evolved by Meadow Grass.* — A section of turf in a dish, floating on water impregnated with carbon dioxide, was placed under a bell-jar and exposed in an open place. Each day new impregnated water was added from a funnel above and the same amount removed from the pan. At the end of a week the air in the bell-jar "was four percent purer than the air of the atmosphere". Illustration from DAVY's "Elements of Agricultural Chemistry", First Edition, London, 1813.

is, however, objectionable as the most useful part of the manure is thus destroyed (p. 263). For this reason DAVY advocates the ploughing under of fresh manure that the fermentation and consequent production of heat may take place beneath the soil.

"In fermentation beneath the soil, the fluid matter produced is applied instantly, even whilst it is warm, to the organs of the plant, and consequently is more likely to be efficient, than in manure that has gone through the process" (p. 265).

DAVY's hypothesis that crops derived much of their nourishment through their roots from the soluble organic constituents of decomposed vegetable and animal matter was especially sponsored by MULDER, three decades later. DAVY's experiments upon the growth of plants in solution of sugar "though not quite decisive, favor the opinion that soluble matters pass unaltered into the roots of plants" (p. 236).

Among mineral fertilizers DAVY discusses the action of calcium carbonate, quick lime, slacked lime, dolomite, gypsum, peat ashes, calcium phosphate and numerous salts of sodium, potassium, and ammonium, with many of which he conducted crop experiments. The favorable action of quick lime upon certain soils is explained by DAVY as due to its tendency of bringing "any hard vegetable matter that it contains into a state of more rapid decomposition and solution, so as to render it a proper food for plants" (p. 278). DAVY accepts the conclusions of DE SAUSSURE that plants are unable to form any of their ash constituents by synthesis or transmutation.

"As the evidence on the subject now stands, it seems fair to conclude, that the different earths and saline substances found in the organs of plants, are supplied by the soils in which they grow; and in no cases composed by new arrangements of the elements in air or water" (p. 273).

In the concluding lecture of his book DAVY discusses the chemical principles involved in the care of pastures and in the improvement of land by burning, irrigating, fallowing, and crop rotation. The chemistry of animal nutrition and of crop utilization are not considered as parts of his subject. The chemistry of the atmosphere, soils, fertilizers and the growth of crops constitute the proper range of agricultural chemistry, according to DAVY's understanding of the term, and in this respect he adhered closely to the usage of previous writers.

DAVY's "Agricultural Chemistry" owing to the pre-eminence of its author exerted a great influence upon the developments of the science. The popularity of the work is attested by the fact that five English editions had appeared by 1836. A German translation by WOLF was published at Berlin in 1814 and American editions appeared at New York in 1815 and at Philadelphia in 1821. An Italian translation under the title, "Elementi di chimica agraria" was published at Florence in 1815 and a French translation, "Éléments de chimie agricole" appeared at Paris in 1819 with a supplement upon the art of making wine and distilling brandy by A. BULOS. The latter work, with its addition of chemical-technological matter not included in the original work, indicates a growing desire at this period to extend the field of agricultural chemistry beyond the confines of a purely agronomic science, so as to include other miscellaneous applications of chemistry to farm operations.

DAVY consulted over one hundred authorities in the preparation of his "Elements of Agricultural Chemistry" and while his digest of previous works represents upon the whole a good summary of the best obtainable knowledge, his support of the hypothesis, against the better judgment of DE SAUSSURE, that plants derived their nutriment chiefly through their roots from the soluble carbonaceous matter of humus, dung, urine, oil, soot and other organic matter of the soil, was a serious blunder which greatly retarded the progress of the science. In this respect, however, DAVY erred in good company for BERZELIUS and other eminent authorities held a similar opinion.

By calling attention in his fourth lecture to the importance of specific gravity, heat capacity, moisture absorptive power and other physical properties in the examination of soils, DAVY was among the first to emphasize the importance of such measurements in agricultural chemical research. This branch of soil science was afterwards developed more considerably by SCHÜBLER. DAVY also rendered a service in stressing the importance of studying the rocks and strata from which soils are derived. His "Elements", although a work of far less importance than the "*Recherches chimiques sur la végétation*" of DE SAUSSURE, is a treatise to which students of the history of agricultural chemistry must always refer.

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Augustin Pyrame de Candolle (1778-1841):—Agricultural chemistry from its first inception has stood in closest relationship to plant physiology and indeed without the constant cooperation of scientific men, who specialized in the study of the nutritive, assimilative, and other physiological processes of plants, agricultural science would have suffered a very imperfect development. Although the contacts between chemists and plant physiologists were at first somewhat hostile, the few investigators who, like STEPHEN HALES, were endowed with both a chemical and physiological viewpoint, did much towards healing some of the early antagonisms. The great reconciler of the opposing chemical and plant physiological schools was the celebrated Swiss botanist, A. P. DE CANDOLLE.

DE CANDOLLE was born at Geneva, in the college of which he began his study of science and particularly of botany, the chief pursuit of his future life. In 1796 he went to Paris to continue his botanical studies and at the early age of twenty-one published his "*Historia Plantarum Succulentarum*," a work in four volumes that won him the immediate recognition of the great naturalists CUVIER and LAMARCK. In 1804 he obtained his medical degree at the University of Paris. His thesis on the medical properties of plants as related to their exterior forms and natural classification indicated the breadth of interests which he displayed in all his future writings. In 1807 he was appointed professor of botany in the medical

faculty of the University of Montpellier. He spent his summers during this period in making a botanical and agricultural survey of France. In 1816 he returned to Geneva and was there appointed to the newly created professorship of natural history, a position which he held until his untimely death at the age of sixty-three. His death was unfortunate as he lived to complete only seven volumes, or two-thirds, of his famous *Prodromus*, or preliminary systematic treatise of the vegetable kingdom.

The part of DE CANDOLLE's work which is of chief interest to the agricultural chemist is found in his "*Physiologie Végétale ou Exposition des Forces et des Fonctions vitales des Végétaux*" (Plant Physiology or an Account of the Forces and Life-Functions of Plants) published at Paris in 1832. It is to this edition that the following citations refer. DE CANDOLLE's various works were written with a carefully planned order of sequence and his Plant Physiology was designed to follow his "Plant Organography" and to precede his "Geographical and Agricultural Botany". In the preface to his Plant Physiology DE CANDOLLE remarks:—

"A part of my youth was devoted exclusively to plant physiology. Up to the present physiologists have especially lacked a detailed acquaintance with organography,—the best means of understanding the published literature, which represents very different points of view. These comprise the opinions in part of men devoted exclusively to the physical sciences without previous physiological studies and consequently without understanding of vital processes; in part of persons devoted entirely to practical horticulture and consequently with an insufficient acquaintance of the laws of organography or of chemistry; and finally in part of men so preoccupied with studies of animal physiology and zoology that they are inclined to exaggerate the relations (very actual within certain limits) between the two organic kingdoms. Without being a physicist or chemist or zoologist or agronomist I have nevertheless devoted some portions of my life to studies in these different professions and I have tried to make an intelligent and impartial application of each one of them to plant physiology" (p. ix).

DE CANDOLLE's "Plant Physiology", a three-volume work of 1579 pages, contains the most complete summary of pre-existing knowledge of plant chemistry that had yet appeared. For its wealth of detailed carefully evaluated historical information (with bibliographic references) it is a work that can still be read with profit by the agricultural chemist.

DE CANDOLLE defines agronomy as the science of agriculture which he divides into eight subsidiary sciences (1) agricultural botany (crops, plant physiology), (2) agricultural zoology (animal husbandry), (3) agricultural chemistry, (4) agricultural physics (meteorology, climatology, etc.), (5) agricultural mechanics (farm machinery), (6) agricultural architecture, (7) agricultural surveying, (8) rural economy (administration, etc.). He defines agricultural chemistry, within its true limits, as that branch of general chemistry which is of use to agriculture (1) directly by teaching soil and fertilizer analysis and especially the art of utilizing the raw materials from which wine, sugar, starch, etc., are made, and (2) indirectly by explaining the processes of plant and animal physiology (Vol. III, pp. 1059-60). The sections of the "Plant Physiology" of chief interest to the agricultural chemist are Volume I, which deals with the nutrition and chemical composition of crops, and Volume III, which deals with the influence of external factors upon the growth of crops such as light, air, water, soil, cultivation, fertilizers, toxic substances, animals, parasites, crop rotation, etc.

DE CANDOLLE's theory of plant nutrition is summarized briefly as follows in the beginning of Chapter 14, Vol. I.

"By the contractile power of the living spongioles of the roots, assisted by capillarity and the hygroscopicity of cellular tissues, the soil solution, with its content of mineral and organic salts, dissolved gases, etc., is absorbed and transported through the intercellular canals of the woody tissues to the leaves. The contractile force of the living cells, and perhaps also that of the canals, is the chief transporting mechanism, assisted also by hygroscopicity, capillarity and the partial vacuum created by transpiration in the leafy tissues. The soil solution in the leaf loses much of its water by evaporation and its content of dissolved substances becomes thereby more concentrated. By the action of sunlight the carbonic acid of the leaf-fluids (whether derived from the soil solution, or the air, or the oxidized carbonaceous matter in the plant) is decomposed, carbon becoming fixed and free oxygen escaping into the air. The first result of this operation is the formation of a gum consisting of one atom of water and one atom of carbon which is then afterwards by very active modifications changed into starch, sugar, and woody tissue (lignine)—materials of very similar composition. The nutritive juice (*suc nourricier*) thus formed, with its content of primary gum, etc., descends from the leaves towards the roots at night, giving up on the way a part of its nutritive matter to the living cells which elaborate it into starch, sugar, gum, woody tissue, fixed oil, etc., which are then either stored up as such or else transported later to nourish other organs of the plant. The nutritive juice in its descent also comes in contact with certain glands which change a part of its dissolved substance into special products, such as resin, which for the most part have no nutritive function and are eliminated from circulation" (pp. 420-2).

DE CANDOLLE was not a firm believer in the mineral theory of manures and attributed the fertility of soils in most part to their content of organic matter. He remarks in this connection:—

"I do not by any means deny the influence of the mineral matter of the soil (*terrain*) but only say that it has been much exaggerated, that if it is a true agent of nutrition it must be referred to special cases and finally that the greater part if not all the facts relative to this subject can be explained as well by the influence of the earths (*terres*) upon the consistence or humidity of the soil as by a special nutritive property which is attributed (I believe without sufficient proofs) to the earths."

"The general rôle of the molecules of organic origin, which are found mixed with the earths in humus-containing soil (*terreau**), is much less ambiguous than that of the earthy matters. These molecules all serve, in different degrees and forms, for the nutrition of plants: (1) they contain a notable amount of carbon under different forms; this carbon is finally resolved into carbonic acid which is dissolved in the water and is absorbed by the roots. (2) This water also dissolves, in greater or less amount, a part of the soluble plant or animal matter which enters the plants and seems to serve evidently for their nutrition" (Vol. III, pp. 1242-3).

DE CANDOLLE's support of the humus theory, because of the high standing of his authority, greatly delayed the acceptance of the mineral theory of plant nutrition.

Another theory, to which DE CANDOLLE gave his unqualified and emphatic support, was that of root exudations. This theory had been proposed previously by BOERHAAVE but it was greatly amplified by DE CANDOLLE who used it as a means of explaining sterility of soils, injurious action of weeds, benefit of crop rotations, and other agronomic phenomena. He dwells repeatedly upon this supposed function of the roots:—

* A careful distinction must be made between the similar French words *terre* (mineral earth), *terrain* (the soil derived from mineral earth), and *terreau* (fertile humus-containing soil.)

"In considering the downward flow of the juices proper and the nutritive juice, we are led to believe that these juices, which direct their course always towards the roots, finally end their course by exuding from their extremities. I had long ago satisfied myself by experiment that healthy roots exhale no gas under water either in light or in darkness, but called from these observations by other demands I did not investigate the nature of the materials which roots excrete in the soil. Ever since 1805 I have called attention to this knotty subject and have often asked different chemists to take up this investigation which, as we will see later, is related to the most important theories of agriculture. Finally my colleague, Monsieur MACAIRE, kindly consented, at my request, to make some efforts to determine the nature of these excretions" (Vol. I, pp. 248-9).

MACAIRE found that living cultures of certain plants in pure rain water imparted to the latter traces of organic matter which precipitated lead acetate solution and left a reddish brown residue on evaporation. Dead twigs and roots of the same plants produced no such effect from which DE CANDOLLE concluded that excretion is a function only of the growing plant. He then continues: —

"These excretions evidently serve to free the living plant of materials which it cannot assimilate or which could injure its health. Mons. MACAIRE has again proved by experiment that by this process plants can actually throw off a part of the poisonous substances which they have absorbed. He placed a plant of annual mercury in such a way that its roots, after being well washed, were placed one part in water containing lead acetate and the other part in pure water. This water, at the end of some days, was found to contain a perceptible amount of lead acetate which was evidently rejected by the plant after having been absorbed through the other part of the roots" (Vol. I, pp. 250-1).

These experiments of MACAIRE, which favorably impressed LIEBIG and other writers, were criticized by later investigators as being faulty in technique. The decline in yield of the same crop when grown several years in succession upon the same field was explained by DE CANDOLLE as a result of injury by toxic root exudations. A different crop, to which the exudations of another species are not toxic, might, however, be grown with good success. This observation led DE CANDOLLE to distinguish between soil exhaustion (*épuisement*) and specific sterility (*effritement*).

"Exhaustion holds true for all crops; it acts by impoverishing the soil through removal of its nutritive matter. Specific sterility is something more special; it acts by corrupting the soil and, as we have indicated in our discussion of root excretions, by contaminating it with a poisonous substance. Thus a peach tree injures a soil for itself in such a way that if without changing the soil a peach tree be replanted in a place, where another has formerly grown, it sickens and dies whereas any other kind of tree would live. The reason why the same tree does not suffer this fate is because its own roots, always extending their growth, constantly meet new veins of earth where their excretions have not yet been deposited. It is conceivable that its own excretions should injure it almost as if an animal should be forced to feed on its own excreta" (Vol. III, pp. 1496-7).

The injurious action of certain weeds, such as spurge, wild poppy, louse-wort, etc., upon neighboring plants was also explained by DE CANDOLLE as a result of toxic root exudations. He held, however, that root exudations of some plants, as the legumes, might be very beneficial to other crops, such as the cereals and in this way explained the benefits derived from clover, lucerne, etc., when grown in rotation.

"It is a ticklish subject for research," he remarks, "but so important that I venture to urge chemists to study the nature of the excretions of different plants in the soil. I have little doubt that careful experiments, directed to this purpose, will prove that soil where the poppy, spurge, chicory, etc. have grown contains acrid substances injurious to vegetation; that soil where legumes, and perhaps cereals, have grown contains sweet mucilaginous substances; that certain families of plants yield excretions of so feeble activity that their action upon the soil can be neglected, whereas others supply them abundantly and of high potency" (Vol. III, p. 1499).

DE CANDOLLE's theory of root exudations was a very elastic one which he stretched almost to the breaking point. It was adopted by SPRENGEL, it was approved by LIEBIG, and even in comparatively recent times it was accepted by WHITNEY in the work of the U. S. Bureau of Soils. Modifications of his theory still find acceptance in modern textbooks.*

DE CANDOLLE did not limit the injurious or beneficial action of plants to their root exudations alone but he extended it to the plants themselves when plowed under as a green manure.

"The effect of this kind of manure," he remarks, "may be either beneficial or injurious to succeeding crops according to the chemical nature of the plants plowed under. Thus, the effect will be useful to most crops, if the plants plowed under contain much substances that are gummy, starchy, saccharine or ligneous, or in general materials that are not acrid; on the contrary the general effect will be injurious if the plants plowed under contain much substances that are acrid, astringent, alkaline, bitter, etc. Thus farmers know very well that they improve the soil by plowing under cereals or legumes and that they injure it, on the other hand, by plowing under poppies or spurges" (Vol. III, pp. 1490-1).

DE CANDOLLE's supposition that certain plants on decay may yield substances that are injurious to crops has been partially verified by the work of SCHREINER and his coworkers of the U. S. Bureau of Soils who have isolated from different soils traces of organic compounds that were definitely toxic to plants. Of the value of the legumes as contributors of nitrogen to the soil and to succeeding rotation crops DE CANDOLLE had not the faintest conception as this phase of plant chemistry was undeveloped in his time.

Of the physiological role of the different mineral constituents of crops DE CANDOLLE had little to say as the technique of studying the effects of withholding this or that ash constituent upon the growth of plants had not been developed. He names lime, magnesia, silica, alumina, barytes, potash, soda, oxides of iron, manganese and copper, chlorine, iodine, sulfur, and phosphorus as having been found in the ashes of plants and, rejecting the views of SCHRADER and of BRACONNOT as to the ability of plants to create or transmute mineral matter, holds that the ash constituents of crops are derived entirely from the soil (Vol. I, pp. 382-91). Of the mineral substances that have been reported to injure plants under varying conditions DE CANDOLLE names compounds of arsenic, mercury, tin, copper, zinc, lead, bismuth, chromium, antimony, iron, calcium, magnesium, barium, aluminum, potassium, sodium, iodine, chlorine, and phosphorus, but in many of the cases cited expressed his uncertainty of the evidence and the need of new investigations (Vol. III, pp. 1328-44). Iron sulfate, copper

* Reference is made to the sections in RUSSELL's "Soil Conditions and Plant Growth," 7th ed., entitled "Excretions of Nitrogen and Mineral Substances from the Roots" (pp. 131-3), "Interactions between Growing Plants" (pp. 553-61) and "Are Toxins present in the Soil" (pp. 561-2).

sulfate, and corrosive sublimate are mentioned as means for destroying weeds (Vol. III, p. 1482).

DE CANDOLLE's discussion of the injury to crops by toxic fumes from chemical works is one of the earliest critical surveys of this important subject. He remarks in this connection:—

"The poisons, which act upon plants by absorption either through the roots or through the leaves, present a difference that seems worthy of notice even from the practical view-point. Experimenters have remarked that poisoning through the roots is most active when the ascent of sap is most rapid and that for this reason it acts more powerfully during the day when the sun shines on the leaves than at night. The opposite should take place with regard to gaseous poisons which act upon the leaves. The latter, in general absorb air only during the night and consequently it is then that the absorption of fumes or deleterious gases should occur with the most force. I believe it is to the difference in the effects of these poisons, by day and by night, that we must attribute the frequent contradiction that is noted in the effects of chemical factories on vegetation and in the experiments employed to determine these. Farmers, near the factories that give off hydrochloric or sulfurous gases, complain that the crops exposed to their action constantly suffer and are often ruined. The manufacturers, citing the experiments of TURNER and CHRISTISON, reply that the amount of deleterious gas, which is customarily present in the air surrounding the factories, is less than that which kills the plants: but this argument is far from being sufficient. Actually (1) we do not have yet any series of proper experiments to determine if a plant, exposed during a long time to an atmosphere containing a very feeble dose of poison, does no suffer as much as from a very strong dose in less time. (2) It is not the average amount of fumes or deleterious gases that must be considered, but the extreme quantity. If a plant is exposed every eighth day to a dose of poison sufficient to affect it, it makes no difference if in the intermediate time it receives a smaller dose. (3) When it is desired to determine the quantity of deleterious gas in the air near factories, the test is made in the day: but during the day the expansion of the air produced by the sun tends to carry the fumes upward, whereas by night they fall towards the earth, like dew or odors, and can thus better attack plants, either in a state of gas or by settling upon the ground. (4) Finally the absorption of these fumes must take place almost entirely during the night. Although there have been many court investigations on this subject I believe it has not yet been realized how much the values of crops are involved, near chemical works or factories that give off deleterious gases" (Vol. III, pp. 1370-2).

Experiments conducted by MACAIRE upon this subject showed that plants exposed to air containing small quantities of chlorine and of fumes of nitrous acid, nitric acid, hydrogen sulfide, and hydrochloric acid, were not affected during the day but suffered appreciable injury at night.

Five chapters (pp. 167-378) of Volume I of the "*Physiologie Végétale*" are devoted to the chemistry of the organic constituents of plants. An extensive abstract of previous investigations in this field is given and the work of over one hundred and fifty chemists is cited with bibliographic references. The number of organic plant compounds which had been isolated up to the year 1830 numbered several hundred. DE CANDOLLE describes no less than 63 vegetable acids and 25 plant alkaloids; his list of carbohydrates, glucosides, tannin substances, coloring materials, resins, oils, waxes, hydrocarbons, albuminous bodies, etc., is also extensive. The elementary composition of many of these organic substances, according to the results of different investigators, is also given by DE CANDOLLE in tabular form.

DE CANDOLLE, although a botanist, was not a narrow specialist. His interests were broad and the interrelations of chemistry, physics, plant

physiology and other sciences with agriculture were indicated more clearly by him than by any previous writer. His works, for their wealth of suggestions, were a source of inspiration to subsequent investigators. The appendix of his *Plant Physiology* contains a long list of suggested researches, which plant anatomists, chemists, physicists, agriculturalists, physiologists and other scientists might undertake for the purpose of widening existing knowledge of plant physiology. The following abstract is given of his suggestions of investigations that needed to be undertaken by chemists (Vol. III, pp. 1527-33).

"Chemistry has rendered immense services to physiology. To chemistry is due the knowledge of the decomposition of carbonic acid and of the principal relations of plants with their surrounding elements: it is chemistry which has taught us to know (1) the elements and (2) the proximate constituents of which plants are formed. The researches of the first class, undertaken for the direct purpose of serving physiology, leave little to be desired; those of the second class, which have been considered almost solely from the view-points of technology or medicine, leave much to be done with regard to studies of the life of plants.

"(A) Many analyses of entire plants have been made without regard to their organs. What conclusions can be drawn in the study of life from analyses made upon complex substances in which all the organs and juices are mixed and which, although perhaps useful in some arts, are completely valueless for physiological purposes? Analysts who wish to make their works valuable from this point of view, must first always distinguish between the different organs and thus work upon products separated from the ligneous substances, the bark, root, branch, leaves, bracts, petals, anthers, fruit, grain, etc. They can easily separate in the woody and barked parts the new and old layers of tissue, the cellular envelope, epidermis, and pith; in the leaves, the veins, petiole, parenchyma, and cuticle; in the anthers, the general envelope, integument of the pollen and fovilla in the fruits, the epicarpe, mesocarpe, endocarpe, pulp and placenta; in the seeds the testa, albumen, germ and cotyledons. Some detailed analyses of different plants, with all their organs thus separated, would render a great service to physiology. Perfecting the art of analysis makes detailed researches possible owing to the possibility of obtaining accurate results with very small quantities of material. But we must not lose sight of the fact that the smaller the scale on which we operate, the more doubtful the result and that microscopic chemistry shares all the errors of atomistic chemistry and of the use of the microscope.

"What I have just said of the organs, is equally true of the juices; the needs of pharmacy have caused separate analyses of them to be made more often, but much remains to be done towards making these analyses more accurate; more efforts must be made towards obtaining pure preparations separated from every admixture.

"(B) Plants have been too often analyzed without the least attention being given to their age or to the vegetative conditions under which the examination was made. Each organ of the plant, analyzed at its first stage of growth, or at middle age, or at maturity, gives different results. The special cases, where this method of successive examination has been tried, have shown its great importance. The gradual transformations of matter during vegetation are thus ascertained and their mechanism, so to speak, can be followed. Similar information would be gained from the analysis of a same organ or of a same juice at different periods of the year and from the analysis of the same plant grown in different soils, environments or climates.

"Under this point of view the chemical researches of THÉODORE DE SAUSSURE on the ashes of plants may serve both as a model of the method to be pursued and as an inspiration of the success that can be expected.

"Chemists have correctly directed their chief efforts towards elucidating the distinguishing characteristics of each one of the proximate constituents of plants; but these constituents are plainly susceptible of modification in the tissue of the living plant and one of the lines of research that will lead most surely to an understanding of plant life is to study the limits of these modifications and the causes which can control them. We already have the proof that several of these constituents can change into one an-

other but this result has been obtained only at high temperatures or by powerful reagents, such as sulfuric acid or caustic alkalis, that cannot be supposed to function in the living plant. Efforts should be directed towards producing these transformations by agencies like those to which the constituents are submitted in the living plant.

"(D) One of the most useful means for ascertaining the limits of these constituent modifications and also for uniting chemistry with botany in their theoretical and practical relations, would be to make comparative analyses of the corresponding organs or juices in a large number of the genera and species belonging to the same natural family. If the same material is found in all, the theories of affinities and of substitutes will be corroborated; if differences are found, then comparisons will lead to a better understanding of the analogy of the components to one another.

"After these considerations of analyses in general, some special projects, that seem worthy of investigation, may be of interest to chemists.

"(1) The subject of starch still presents some knotty problems for investigation. Is its soluble part identical, or only analogous, with gum? Is its integument the same in chemical nature as the envelop proper of cells? To what is the coloration or non-coloration by iodine due in materials that are otherwise much alike? Is it true that the same plant and the same organ, in different circumstances, can give a starch that is colored or not colored by iodine? What are the variations in the quantity of starch in the same organs at different ages?

"(2) It would be useful to make the analysis of woody tissue taken from the same tree at different ages of the ligneous layers so as to make the comparisons at different degrees of lignification; taken from woody trees of very different kinds but at the same age; taken from different organs such as the wood proper, the bark, root, etc.; and finally taken from different classes of plants, such as the endogens and exogens, and also from those cellular plants where it is reported to have been found. The experiments should be conducted so as to distinguish, if it is possible, the cellular membrane from the ligneous deposits that are formed there.

"(3) Determine experimentally the probable acid nature of the juice that enables lichens to etch calcareous stones and that of the substance that enables lichens or algae to adhere so closely to rocks.

"(4) Determine the nature of the caustic juice in the glands at the base of the hairs of nettles, malpighia, *Jatropha brulans*, etc., which probably contains an alkali.

"(5) Determine the characteristic of the glue and glutinous matters excreted by plants.

"(6) Make comparative analyses of the plant waxes, whether excreted by the leaves, buds, fruits, etc., as a glaucous powder, or mixed in the laticiferous juices, etc. Probably different substances are confused under this name.

"(7) Examine the glary coating that covers a large number of aquatic plants and protects them against water.

"(8) Make comparative analyses of the nectars supplied by flowers of different families and by different kinds of nectaries.

"(9) Make comparative analyses of the different juicy exudations known as manna.

"(10) Examine the bitter substance that fills the pods of *Sophora japonica* and of other related leguminosae and compare it with the products of that family long confused under the name of extractive.

"(11) Following the work commenced by MACAIRE, determine carefully the nature and quantity of the substances excreted by roots and deposited by them in the soil; compare the nature of these excretions in the families with sweet juices, as the legumes and cereals, with those having a bitter juice, as the poppies, spurge, etc.

"(12) Analyze the water that forms or gathers in the cavities of the leaves of pitcher plants, as nepenthes, cephalotus, etc., and that which issues from *Caesalpinia pluviosa*.

"(13) Increase the comparative analyses of laticiferous juices first from plants of the same family and then with plants from different families.

"(14) Compare laticiferous juices at different ages. What becomes particularly of that of the fig at the time of maturity? How is a substance so bitter changed or replaced by a substance so sweet?

"(15) Determine the general composition of the resinous juices and classify their

different products by making a greater number of analyses of products from the same and different families.

"(16) Compare with one another and with camphor the different solid substances that separate from essential oils.

"(17) Compare in the same way products similar to the fixed oils both with one another and with the substances known as butters.

"(18) Make comparative studies of the saponaceous substances obtained in the different organs and families of the plant kingdom.

"(19) Does rubber belong to the nitrogenous substances? Is its method of formation dependent upon the influence of the air?

"(20) Is the yellow color of the juice of celandine and of some guttifers due to the presence of some alkaline salt, as is said to be the case with the red color of the juice of bloodwort?

"(21) Repeat the experiments suitable for determining the nature of the air enclosed in the ducts and internal cavities of plants, according to season, time of day, exposure to darkness or sunlight, etc. Is this air particularly more oxygenated than atmospheric air as BISCHOFF states or less oxygenated as DUTROCHET affirms? Is the air of the ducts identical in nature with that of the cavities?

"(22) Determine on a large scale, as MACAIRE has already done on a small one, whether the contradictions that seem to exist between the direct experiments on the effect of noxious fumes and the observations made near chemical works, are not due to the fact that the fumes are absorbed by plants only during the night while the experiments are made during the day?

"(23) Do perfectly blue mushrooms, such as *Telephora caerulea*, contain a noticeable quantity of iron oxide?

"(24) Is there any chemical analogy between the state of leaves that have developed a russet color (feuille morte) and that of bletted fruit?

"(25) Are the perfectly black colors observed in some mushrooms (*Peziza nigra*, *Sphaeria hypoxylon*) or in the dying corollas of *Tournefortia mutabilis* due to some formation of ulmine?

"(26) Would it not be possible to condense and analyze the perfumes exhaled by a large number of flowers?

"(27) Determine the elementary composition of the proximate constituents of plants where it is not known and whether the substances thus analyzed actually deserve to be called distinct."

Many of the chemical problems, suggested by DE CANDOLLE for future research, have since been solved; others still await the attention of the agricultural and physiological chemist. While many of DE CANDOLLE's views were later proved to be extreme or faulty, his broad illuminating outlook, extremely modern in many of its aspects, and his suggestive hints (soupçons) gave a marked stimulus to subsequent research.

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Chapter VII

AGRICULTURAL CHEMISTRY AT THE BEGINNING OF THE MODERN PERIOD

As previously stated the foundation stones of agricultural chemistry were largely provided by the work of LAVOISIER while the placing of these stones in their proper position was chiefly the accomplishment of DE SAUSSURE. It was not, however, until the period 1820-1850 that the structure of modern agricultural chemistry began to assume importance upon the basis of this preexisting work. Developments proceeded very unequally, the contributions of one investigator predominating in one field and those of another elsewhere. Henceforth the progress of agricultural chemistry is to be considered more and more in the light of a general perspective and less and less from the viewpoint of individual contributions.

There were many factors that gave a stimulus to agricultural chemistry during the early decades of its modern development of which only a few need be mentioned. A first very important incentive was the establishment of chemical research laboratories for young students in various European schools and universities. A second factor, closely related to the establishment of these laboratories, was the founding of a number of new journals for publishing the rapidly growing output of the results of chemical research. The publications of DINGLER's "Polytechnisches Journal" in 1820, of BERZELIUS's "Jahresbericht" in 1822, of ERDMANN's "Journal für technische und ökonomische Chemie" in 1828, and of LIEBIG's "Annalen" in 1832, are cited as examples of this movement. As clearing houses of chemical research these and other journals imparted a powerful stimulus to the developments of this period. A third contributing influence was the perfection of new chemical and physical methods for the analysis of soils, fertilizers, crops and animal products. A brilliant example of this development was the application of the polariscope by BIOT in 1842 to the determination of sugar in maize stalks,—a procedure that was immediately made use of in many fields of agricultural analysis. The great extension throughout Europe in the culture of the sugar beet during this period was a fourth important factor. This valuable new crop—one of the greatest gifts of chemistry to agriculture—made growing demands upon this science for increasing its sugar content and for improving the methods of its utilization.

A necessary accompaniment of these newer developments was the demolition of the remnants of certain long-impeding vitalistic ideas. The view that the mineral constituents of plants could be produced by the transmuting activity of their living cells did not receive its final overthrow until the work of WIEGMANN and POLSTORFF which although chronologically later, is treated first since it was largely a confirmation of the previous work of DE SAUSSURE and played no important part in the developments of the modern period.

A. F. Wiegmann (1771-1853):—Notwithstanding the early convincing work of DE SAUSSURE upon the origin of the ash constituents of plants and the later publications of SPRENGEL upon the necessity of the soil containing the mineral constituents which plants require for their proper

development, the conservatism of scientific opinion caused these matters to be regarded by some plant physiologists, even until after 1840, as questions that still awaited proof. As we review today the developments of this period there seems to have been an expenditure of much needless effort in an attempt to prove what had already been proved or disproved. Older writers were frequently ignored or misinterpreted and the errors of one writer were copied by others so that mistakes once perpetrated were often continued for several decades. These oversights are no where more apparent than in the numerous publications, relating to the basic problem of the influence of soils and fertilizers upon plant growth, which appeared during the first half of the nineteenth century.

Following the rule of INGEN-HOUSZ that, "the surest way to find out the real nourishment of organized bodies seems to be, to inquire what is the substance, without which they inevitably perish", experimenters at the commencement of the century began to study the growth of plants in wholly inert substances such as flowers of sulfur, sand, carbon, powdered metals and metallic oxides, etc., from which no nutritive material could be derived. Thus SCHRADER (1800) was awarded a prize by the Berlin Academy of Sciences in 1799 for two papers which he published upon the generation of mineral constituents in different domestic grains. He caused seeds of wheat, barley, rye, etc., to germinate in flowers of sulfur, which was kept moistened with distilled water and sheltered from dust and rain. From his determinations of ash in the seedlings thus produced, SCHRADER concluded that mineral matter was actually created in the plant. Similar conclusions were reached by BRACONNOT (1806) who, growing plants to maturity upon extracted peat, litharge, sublimed sulfur, granulated lead, and quartz pebbles, concluded that "the organic force, assisted by sunlight produces in plants substances, regarded as elementary, such as earths, alkalies, metals, sulfur, phosphorus, carbon and perhaps also nitrogen". BRACONNOT, in fact, justified the conclusion of VAN HELMONT and advocated a return to the ancient conception of THALES that water was the primal substance from which everything was derived; he even suggested, since water is itself a compound, that oxygen, hydrogen, and fire are the only original elements from which the universe was derived.

The strange conclusions reached by both SCHRADER and BRACONNOT as to the existence of a creative transmuting force in plants were a backward step and delayed the adoption of the opinions of DE SAUSSURE. LESSAIGNE (1821) repeated the experiment of growing seeds in purified flowers of sulfur and was unable to discover any increase in the ash content of the plants above that contained in the seeds. He, therefore, defended the views expressed by DE SAUSSURE in 1804. A similar confirmation was also obtained by JABLONSKI (1836). In view, however, of the persistent uncertainty upon this subject a prize was offered in Germany in 1838 for the contribution giving the most satisfactory answer to the questions, "Do the so-called inorganic elements, which are found in the ashes of plants, occur in these plants when exterior sources of these elements are eliminated? Are these inorganic elementary constituents so essential that the vegetable organisms have constant need of them for their complete development?" The prize for the best contribution giving answers to these questions was awarded in Göttingen in 1840 to A. F. WIEGMANN, a professor

Ueber die
anorganischen
Bestandtheile der Pflanzen,

oder

Beantwortung der Frage:

Sind die anorganischen Elemente, welche sich in der
Asche der Pflanzen finden, so wesentliche Bestandtheile des
vegetabilischen Organismus, dass dieser sie zu seiner völligen
Ausbildung bedarf, und werden sie den Gewächsen
von Außen dargeboten?

eine in Göttingen im Jahre 1842

gekrönte Preisschrift,

nebst einem

Anhange über die fragliche Assimilation des Humusextractes

von

Dr. A. F. Wiegmann,

Professor in Braunschweig

und

L. Polstorff,

Administrator der Hofapotheke in Braunschweig

Braunschweig.

Druck und Verlag von Friedrich Vieweg und Sohn.

1842.

FIG. 31. — Title page of WIEGMANN and POLSTORFF's prize-publication "Ueber die anorganischen Bestandtheile der Pflanzen", Brunswick, 1842.

of Brunswick, and L. POLSTORFF, an apothecary of the same city, for their essay "Ueber die anorganischen Bestandtheile der Pflanzen . . . nebst einem Anhang über die fragliche Assimilation des Humusextractes" (On the Inorganic Constituents of Plants . . . with an appendix on the disputed Assimilation of Humus-extract).

The investigations of WIEGMANN and POLSTORFF were of such a conclusive character that just criticism of the correctness of the views expressed by DE SAUSSURE in 1804 as to the origin and importance of the mineral matter of plants was forever silenced. It is to the original publication of WIEGMANN and POLSTORFF (1842) that the following citations refer.

Previous to undertaking his experiments WIEGMANN, as a result of reading the publications of DE SAUSSURE, LESSAIGNE, JABLONSKI, and other investigators, and especially of SPRENGEL (1828-33) and of LAMPADIUS (1832), had become convinced that plants for their complete development require a definite quantity of certain inorganic constituents and that these assimilated mineral elements, which reappear in the ashes of plants, are derived entirely from without, in large part from the soil and to a much lesser extent from atmospheric sources, such as dust, rain, and snow. In order to confirm this belief he adopted a somewhat different technique from that employed by his predecessors.

Taking SPRENGEL's analysis of a fertile soil as a basis, he prepared a synthetic soil of somewhat similar composition consisting of a mixture of purified quartz sand with calcium phosphate, alumina, calcium carbonate, magnesium carbonate, ferric oxide, manganic oxide, burned gypsum, potassium sulphate, sodium chloride, insoluble humus, and the mixed humates of potash, soda, lime, magnesia, iron, alumina, and ammonia. In pots of this synthetic soil and in comparison pots of sand alone he planted seeds of vetch, barley, oats, buckwheat, tobacco, and clover. The pots were protected from atmospheric contaminations and were regularly watered with twice distilled water. At the end of maximum growth the plants of each pot were harvested with leaves, stalks and roots (the latter being washed with distilled water to remove all adhering soil), dried, incinerated and the ash of each sample weighed and analyzed. The following is a partial tabulation of the results: —

PERCENT ASH IN DRIED PLANTS CORRECTED FOR WEIGHT OF ASH IN ORIGINAL SEED

Plant	Grown in Sand	Grown in Synthetic Soil
	<i>Percent</i>	<i>Percent</i>
Tobacco	12.60	18.20
Vetch	6.32	11.71
Clover	5.67	10.66
Barley	4.80	6.40
Oats	3.90	5.07
Buckwheat	1.60	3.63

(*loc. cit.*, pp. 18-27).

The table shows that of the plants studied tobacco was the strongest in its demands for mineral matter and buckwheat the weakest. The plants

grown in sand were stunted, sickly and failed to seed; those grown in synthetic soil grew luxuriantly and seeded normally. The sand employed in the experiments was analyzed and found to contain silica 97.900%, alumina 0.876%, lime 0.484%, potash 0.320%, ferric oxide 0.315%, magnesia 0.009%, undetermined 0.096%. The gain in ash of the plants grown on sand above the ash contained in the seed was attributed by WIEGMANN to the assimilation of traces of mineral matter from the sand by the rootlets of the plants. The results showed conclusively that a deficiency of available mineral matter in the soil results in the failure of crops to make a normal growth.

While these experiments were conclusive in so far as they went, the old hypothesis, persisting for centuries, that plants had the power of generating mineral matter by the transmuting activity of a vital force had not been completely disproved. In order to settle this question and to remove all doubt of the experimental plants absorbing mineral matter from glass or earthenware WIEGMANN selected as his containing vessel a large platinum crucible and as his inert substitute for soil a porous mass of fine platinum wire, kept moist with distilled water, in which were planted seeds of garden cress (*Lepidium sativum*). The crucible was placed under a bell jar through which was circulated a synthetic gas mixture consisting of 21 volumes of oxygen, 78 volumes of nitrogen and 1 volume of carbon dioxide. The seeds germinated and the plantlets grew for 26 days when they began to turn yellow and die. The 28 plants thus obtained were dried, weighed and incinerated. The weight of ash obtained was 0.0025 gram; the weight of ash obtained from 28 seeds was also 0.0025 gram. There was, therefore, no production of new mineral matter within the plant. As a result of their experiments WIEGMANN and POLSTORFF drew the following conclusions: —

"(1) Plants can subsist for a time upon the reserves of inorganic materials contained in the seeds from which they germinated, but growth ceases as soon as these reserves become insufficient to supply the vegetative needs.

"(2) The inorganic constituents of plants can in no respect be regarded as products of their vital activity either as formations from unknown elements or as peculiar derivatives of the four elements known to make up organic substances.

"(3) If plants are shut off from all exterior sources of inorganic matter, then the amount of the latter which they contain cannot exceed the quantity originally present in the seeds (*loc. cit.*, pp. 35-6).

Thus, after a period of over 35 years of alternating proof and disproof, the correctness of the views promulgated by DE SAUSSURE in 1804 was finally established beyond all possibility of doubt.

WIEGMANN and POLSTORFF also disproved (pp. 37-8) the supposition that mineral matter is generated during the alcoholic fermentation. They also criticized the opinion that the declining productivity of a field upon which the same crop has been grown continuously is due to an accumulation of toxic root excretions. WIEGMANN's experiments of 1834 and 1838 (*loc. cit.*, p. 49) failed to confirm the findings of MACAIRE-PRINSEP (1833) as to the existence of such exudations and the work of WALSNER in Tübingen gave a similar negative result (*loc. cit.*, pp. 48-9). In this connection WIEGMANN remarks: —

"The well established observation, that cultivated plants seldom thrive perfectly if they are grown again upon the same soil on which similar crops were produced the previous year . . . has also been attributed to the action of root exudations. It has been asserted in fact that just as an animal cannot thrive upon its excreta, so a plant is unable to thrive upon the exudations of its own kind although plants of another family can utilize them as food and manure.

"It has been overlooked, however, by those who adopt this view that injurious organic exudations are destroyed by fermentation, that harmful inorganic ones, by being plowed under and mixed with other substances of the soil, are rendered innocuous and finally that trees flourish luxuriantly on their ejecta several hundred, yes even a thousand years.

"The above mentioned observation of farmers and gardeners is much more simply explained by supposing that the soil has been so robbed by the previously harvested crop of the inorganic materials which are necessary for plant development that another crop of the same kind (even when the ground is plowed and newly fertilized with an animal manure deficient in the necessary mineral element) is unable to find the requisite amount of plant food that is necessary for its complete development" (*loc. cit.*, p. 50).

In an appendix (pp. 52-5) to their publication WIEGMANN and POLSTORFF describe an experiment upon the growing of plants in humus extract. The residue in 100 grams of extract exposed to the air for a month was 136 milligrams; the residue in 100 grams of extract in which the plants had grown for a month was 132 milligrams. Because of this slight difference the authors concluded that humus plays an insignificant rôle in plant nutrition.

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Gustav S. Schübler (1787-1834):— A new approach to the problems of agricultural chemistry was given by Professor G. SCHÜBLER, of the University of Tübingen, who was the first to devote careful attention to the physical properties of soils, fertilizers, and crop constituents in connection

G r u n d s ä t z e
der
Agricultur = Chemie
in näherer Beziehung auf land- und forstwirth-
schaftliche Gewerbe

von
G. Sch ü b l e r,
ordentlichem Professor an der Universität zu Tübingen, mehrerer gelehrten Gesells-
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1 8 3 0

FIG. 32 — Title page of SCHÜBLER's "Grundsätze der Agricultur-Chemie", Leipzig, 1830.

with methods for their classification and evaluation. He was born at Heilbronn, Germany, where he obtained his first instruction. After completing his preparatory education at the gymnasium of Ellwangen, he went in 1806 to Tübingen where he took up the study of medicine and the natural sciences. He completed his medical education at Vienna and in 1811 began practice, as a physician, in Stuttgart. In 1812 he accepted a call by P. E. VON FELLEBERG to teach science at the new agricultural institute which he had established at Hofwyl, near Bern, Switzerland. This institute, which VON FELLEBERG founded with the double purpose of training pupils of both high and low estate in the science and practice of agriculture and in moral discipline, became a noteworthy one and pupils were attracted from all countries of Europe. It was here that SCHÜBLER's interests in agriculture were first aroused. SCHÜBLER remained with VON FELLEBERG until 1817 when he accepted an appointment as professor of botany and natural science on the medical faculty of the University of Tübingen, where he remained until his brilliant career, as investigator, teacher and writer, was terminated by a heart attack at the early age of forty-seven.

Although he is best known for his work in botany, SCHÜBLER is chiefly remembered by agricultural chemists for his "Grundsätze der Agriculturchemie in näherer Beziehung auf land- und forstwirthschaftliche Gewerbe" or "Fundamentals of Agricultural Chemistry with special reference to practical farming and forestry", which was published in 1830. This work is interesting for the viewpoint which SCHÜBLER maintains as to the relationship of agricultural chemistry to other sciences and especially to general chemistry. This is indicated at the beginning of his introduction to the First Part of his Agricultural Chemistry which is entitled, "Fundamentals of Chemistry as an Introduction to the separate branches of agriculture, the arts and crafts, and the whole general field of domestic science". After showing the distinction between chemistry and physics and between pure and applied chemistry SCHÜBLER discusses the relations of chemistry to domestic science and agriculture (*Verhältnisse der Chemie zur Haus- und Landwirthschaft*): —

"Each single division of chemistry presupposes a knowledge of the laws of general chemistry without which many phenomena cannot be explained. Agriculture itself and most of the practical branches of domestic science and husbandry depend upon chemical fundamentals. A chemistry of domestic science and husbandry, or Agricultural Chemistry in the broad sense of the word, must therefore present the fundamentals of general chemistry in simple understandable language and must also consider the various materials which are related to domestic science and husbandry and their ordinary practical applications. It must besides, in the case of these individual materials, indicate the important uses to which they are put in order to provide a better introduction to the separate branches and applications of agricultural science.

"The discussion of the simpler earths and their chemical relationships to one another belongs to the more general preliminary chemistry of domestic science and agriculture; the way in which the different kinds of soil are resolved, belongs to Agronomy. The discussion of fermentation in general belongs to this introductory part; the art of distilling alcoholic spirits on the other hand belongs to technical chemistry" (*loc. cit.*, pp. 2-3).

We have in this introductory statement of SCHÜBLER one of the first examples of an effort to systematize the growing complexities of agricul-

tural chemistry which was beginning to acquire the status of a heterogeneous mixture of chemistry and other sciences and of various special applications of chemistry to agriculture and to the utilization of farm products. The discussion of the laws of general chemistry which are essential to an understanding of agricultural chemistry are, therefore, set off by SCHÜBLER as the first part of his book (240 pages). The physical properties and chemical constitution of soils, fertilizers, and the plant products obtained in agriculture and forestry form the second part of his book (238 pages) which is entitled Agronomy.

In the first introductory part of his treatise SCHÜBLER gives an excellent summary of the main facts, as then known, of inorganic and organic chemistry with special reference to the mineral, plant and animal substances related to agriculture, such as lime, potash, sugars, starches, oils, fats, organic acids, alcohol, natural dyestuffs, etc., with brief mention of their chemical properties and uses.

The second half of the volume, which deals with what SCHÜBLER terms agronomy, is the part of chief interest to the agricultural chemist. Under agronomy, however, SCHÜBLER included much more than is considered by modern writers in their treatment of the subject, as can be seen from the following brief abstract of the six sections which he grouped under this designation: —

SECTION I. *Constituents of Soils* (pp. 1-56).

- A. Stable constituents: (1) pebbles, rock particles, etc.; (2) different kinds of sands; (3) clay and other fine elutriable particles.
- B. Decomposable and occasional constituents (humus; remains of plant and animal origin; particles of gypsum and other crystalline salts).

SECTION II. *Physical characteristics of soils and methods for their determination* (pp. 57-94).

(Determination of specific gravity, hygroscopic power, plasticity, drying capacity, heat retention, changes in volume, water absorption, etc.).

SECTION III. *Chemical examination of soils* (pp. 95-134).

(Methods for sampling; methods for determining moisture; water-soluble matter; sand; clay; lime; magnesia and other bases; phosphoric, sulfuric, and other acids; humus; carbon dioxide; tables of 48 soil analyses; discussion of results).

SECTION IV. *Subdivision and classification of soils* (pp. 135-52).

- A. Physical classification (heavy soils, light soils, etc.).
- B. Geognostic classification (calciferous, quartziferous, granitic, etc.).
- C. Chemical classification (according to preponderance of clay, sand, loam, marl, humus, etc.).

SECTION V. *Fertilizers* (pp. 152-70).

- A. Vegetable fertilizers (composts of straw, leaves, weeds and other refuse; oil-cakes; peat; green-manuring, etc.).
- B. Animal fertilizers (solid and liquid excreta; bones; blood; tankage, etc.).
- C. Mineral fertilizers (slaked lime; marl; ashes; gypsum; burnt clay, etc.).

SECTION VI. *Constituents of the more important plant products* (pp. 171-238).

- A. Obtained in agriculture (percentages of starch, sugar, bran, oil, gum, albumen, phosphate, etc., in different grains, seeds, vegetables, fruits, juices, grasses, root crops, etc.; effects of different fertilizers on yields of these constituents).
- B. Obtained in forestry (saps, gums, resins, turpentine, barks, tannins, dyestuffs, etc., obtained from trees; water and ash content, and specific gravity of different woods; yields of charcoal, tar, pyroligneous acid and inflammable gas from destructive distillation of woods, etc.).

Details of sugar manufacture, of alcohol distillation, and of other technological processes; discussions of national economics (such as occur in the works of CHAPTAL); and the nutrition of farm animals are not considered by SCHÜBLER in his "Grundsätze der Agricultur-Chemie".

SCHÜBLER can be called the founder of soil physics and his extensive tabulations of the physical properties of different soils and soil constituents can still be consulted with profit. A few examples of his work in this field are quoted.

SUBSTANCE: —	SPECIFIC GRAVITY (WATER=1 AT 4.1°C)	WEIGHT OF ONE PARIS CUBIC FOOT IN NÜREMBERG POUNDS	
		DRY CONDITION	WET CONDITION
Quartz sand	2.653	111.3	136.1
Sandy Limestone	2.722	113.6	141.3
Earthy gypsum	2.331	91.9	127.6
Powdered calcium carbonate.....	2.468	53.7	103.5
Powdered magnesium carbonate....	2.194	15.8	76.3
Potter's clay	2.601	97.8	129.7
Loamy clay	2.581	88.5	124.1
Pure gray clay.....	2.533	75.2	115.8
Humus	1.370	34.8	81.7
Loam of cultivated field.....	2.401	84.5	119.1

(SCHÜBLER'S Grundsätze, Part II, p. 60.)

SUBSTANCE: —	WATER RETAIN- ING POWER	HYGROSCOPICITY (1000 PARTS OF DRY SUBSTANCE ABSORBED IN WATER SATURATED AIR)			
		12 HOURS	24 HOURS	48 HOURS	72 HOURS
		Percent by weight	1000 parts	1000 parts	1000 parts
		1000 parts	1000 parts	1000 parts	1000 parts
Quartz sand	25	0	0	0	0
Sandy limestone	29	2	3	3	3
Earthy gypsum	27	1	1	1	1
Powdered calcium carbonate.....	85	26	31	35	35
Powdered magnesium carbonate....	256	69	76	80	82
Potter's clay	40	21	26	28	28
Loamy clay	50	25	30	34	35
Pure gray clay.....	70	37	42	48	49
Humus	181	80	97	110	120
Loam of cultivated field.....	52	16	22	23	23

(SCHÜBLER'S Grundsätze, Part II, pp. 65, 81.)

SUBSTANCE: —	CHANGE IN VOLUME ON DRYING	STICKINESS OF WET SUBSTANCE	
	1000 PARTS WET SUBSTANCE DIMINISHED ITS VOLUME BY	POUNDS RETAINED BY ONE SQ. FT. OF IMPLEMENT	
		IRON SURFACE	WOOD SURFACE
Quartz sand	0 parts	3.8	4.3
Potter's clay	60 "	7.9	8.9
Pure gray clay.....	183 "	27.0	29.2
Humus	200 "	8.8	9.4
Loam of cultivated field.....	120 "	5.8	6.4

(SCHÜBLER's Grundsätze, Part II, pp. 79, 74.)

SUBSTANCE :—	DRYING CAPACITY			HEAT RETENTION		
	100 PARTS OF AB- SORBED WATER	TIME REQUIRED		HEAT RE- TENTION OF SANDY LIMESTONE = 100	TIME FOR 30 CUBIC INCHES OF SUBSTANCE TO COOL FROM 50°R TO 17°R AT A TEMPERA- TURE OF 13°R	
	LOST BY EVAPORA- TION IN 4 HOURS AT 15°R	FOR 100 PARTS ABSORBED WATER TO LOSE 90 PARTS AT 15°R				
	100 parts	Hours	Minutes		Hours	Minutes
Quartz sand	88.4	4	4	95.6	3	20
Sandy limestone	75.9	4	44	100.0	3	30
Earthy gypsum	71.7	5	1	73.8	2	34
Potter's clay	52.0	6	55	76.9	2	41
Loamy clay	45.7	7	52	71.8	2	30
Pure gray clay.....	31.9	11	17	66.7	2	19
Powdered calcium carbonate...	28.0	12	51	61.3	2	10
Powdered magnesium carbonate	10.8	33	20	38.0	1	20
Humus	20.5	17	33	49.0	1	43
Loam of cultivated field.....	32.0	11	15	70.1	2	27

(SCHÜBLER's Grundsätze, Part II, pp. 77, 86.)

SCHÜBLER's influence on succeeding developments of agricultural chemistry was immediate. His processes for the physical examination of soils were at once adopted by SPRENGEL, BOUSSINGAULT, and other writers and his methods, or their modifications, soon became a part of the regular procedure in all agricultural chemical laboratories.

The work of SCHÜBLER was perpetuated in that of his students. In the Library of Congress are twelve inaugural dissertations (4 in Latin and 8 in German) by students who obtained their Ph.D. degrees under SCHÜBLER at Tübingen between 1818 and 1832. Several of them relate to his favorite field of physical measurements, such as temperature changes in plants, specific gravities of seeds and other plant organs and color and odor relationships of plants.

REFERENCE:—

SCHÜBLER, G. (1830): Grundsätze der Agricultur-Chemie in näherer Beziehung auf land- und forstwirthschaftliche Gewerbe. Ein integrierender Theil der allgemeinen

Encyklopädie der gesammten Land- und Hauswirthschaft der Deutschen. Leipzig, Baumgärtners Buchhandlung.

Carl S. Sprengel (1787-1859): — Among the many agricultural chemists who preceded LIEBIG there was no one so widely acquainted with practical husbandry in its various branches as SPRENGEL. He was born at Schillerslage near Hannover, Germany, and after leaving school spent seven years with THAER at Celle and Möglin in the study of agriculture. It was here under EINHOF that he obtained his first training in agricultural chemistry. SPRENGEL then served for seven years as manager of several large estates in Saxony and Silesia after which he made a long agricultural tour through Germany, the Netherlands, France and Switzerland. From 1820 to 1824 he studied chemistry and other sciences at Göttingen University where he served afterwards until 1831 as instructor in agriculture and agricultural chemistry.

A prospectus of the courses of SPRENGEL (1829) at Göttingen in agricultural chemistry and related subjects has considerable historic interest. In addition to laboratory instruction in the analysis of soils, fertilizers and crops he taught the elements of agronomy and other phases of applied agriculture. He conducted excursions to familiarize students with soil types, irrigation of fields, crop rotation, reclamation of land, use of implements, cattle raising, and good and bad systems of farm management. Theoretical instruction went hand in hand with practical training.

In 1831 SPRENGEL was appointed professor of agriculture and agricultural chemistry at the Collegium Carolinum in Brunswick, a position which he resigned in 1839 to become general secretary of the Pommeranian Economic Society at Regenwald where he established an agricultural academy and a factory for making agricultural implements. He died at Regenwald in April 1859, lamented by many devoted students whom he had trained and by numerous European agricultural societies of which he was an honorary member. SPRENGEL had not only a comprehensive grasp of practical agriculture but he was a tireless investigator and author. It is strange that his name should have been so completely overlooked by later writers, although he was the first to announce many of the ideas that have been wrongly accredited to LIEBIG and other later investigators. If some of his opinions had won immediate recognition, the science of agricultural chemistry would have been greatly advanced.

During his Göttingen period SPRENGEL began publishing in various journals a long series of important articles on different phases of agricultural chemistry. He was a man of independent judgment and a deep student of the works of DE SAUSSURE and SCHÜBLER to whom he expressed repeated indebtedness. Although assimilating much of THAER's teaching in practical agriculture he completely broke with this authority with regard to the supposed genesis and transmutation of mineral elements within the plant. In his first noteworthy contribution on "Plant humus, humic acid and its salts" SPRENGEL (1826a) expressly denied the capacity of plants to form lime and other non-combustible ingredients. He held with DE SAUSSURE that the mineral elements of plants are derived from without and that when these supplies are carefully excluded the mineral content of the young plant cannot exceed that of the seed from which it germinated. The ap-

parent exceptions to this, noted by SCHRADER and others, he attributed to mineral impurities derived from the water or air.

In 1828 SPRENGEL began a series of important articles upon soils, manures, crops and other agricultural chemical subjects which he continued through volumes 2 to 17 (1828-33) of ERDMANN'S "Journal für technische und ökonomische Chemie". These articles, 37 in number, received the warmest praise from LAMPADIUS and other chemists. They were afterwards assembled by SPRENGEL and made the basis of several of his books.

Of the numerous books published by SPRENGEL the following are of chief importance: "Chemie für Landwirthe, Forstmänner und Cameralisten" (Chemistry for Farmers, Foresters and Cameralists) published in two volumes at Göttingen in 1831-32; "Die Bodenkunde oder die Lehre vom Boden nebst einer vollständigen Anleitung zur Chemischen Analyse der Ackererden" (Soil Science or a Treatise on the Soil with a complete Introduction to the Chemical Analysis of Cultivated Soils), published at Leipzig in 1837 (2nd edit. 1844); "Die Lehre von den Urbarmachungen und Grundverbesserungen" (The principles of Land Reclamations and Improvements) published at Leipzig in 1838 (2nd edit. 1846); "Die Lehre vom Dünger oder Beschreibung aller bei der Landwirthschaft gebräuchlicher vegetabilischer, animalischer und mineralischer Düngermaterialien nebst Erklärung ihrer Wirkungsart" (Principles of Fertilization or a description of the vegetable, animal and mineral fertilizers employed in agriculture with an explanation of their mode of action), published at Leipzig in 1839 (2nd edit. 1845); and "Meine Erfahrungen im Gebiete der allgemeinen und speciellen Pflanzen-Cultur" (My experiences in the field of general and special crop-cultivation), Leipzig, Vol. 1 (1847), Vol. 2 (1850), Vol. 3 (1852).

Of the various sciences involved in the study of agriculture SPRENGEL regarded chemistry as of most importance. In the introduction of his "Lehre von Urbarmachungen" (First Edit. 1838, pp. iv-v) he remarks:—

"My critics will most probably accuse me of again overestimating the importance of chemistry but such complaints I quietly dismiss since I am most firmly convinced that here again it is chemistry that indicates to us most correctly the way which we should adopt in most improvements of the land. I must more than ever ascribe a great rôle to chemistry since only with its help have I been able to explain in a completely satisfactory way the many puzzling phenomena that occur in the improvements and reclamation of land. . . . Of chemistry in general I gladly confess that I would have obtained far greater success not only in land improvements and reclamation but also in the entire field of agriculture, had I possessed as good a knowledge of this most eminent of all sciences at the beginning as I have now."

SPRENGEL'S appreciation of the importance of chemistry to agriculture did not limit his outlook, however, to strictly chemical aspects. He realized that a study of husbandry involves a broad knowledge of many sciences and his works discuss the mutual relationships to agriculture of chemistry, physics, geology, meteorology, plant physiology, mechanics and engineering.

In all his various works SPRENGEL emphasizes the need of crops in obtaining from air and soil all of the chemical elements necessary for their proper growth and maturity. The 15 elements regarded by him as essen-

tial for the growth of plants are oxygen, carbon, hydrogen, nitrogen, sulfur, phosphorus, chlorine, potassium, sodium, calcium, magnesium, aluminum, silicon, iron, and manganese (Dünger, 1845, pp. 45-6). He remarks that other elements not yet discovered, as fluorine, iodine, bromine, lithium, and copper, may also be found to be essential, even though they may occur in only minute amounts (*loc. cit.*, p. 49), a statement foreshadowing the modern discovery of trace elements. The first three of the elements named are supplied largely from the air and the remaining twelve from the soil. If only one of the elements necessary for growth be lacking, the plant will not thrive, even though all of the others occur in abundance. SPRENGEL thus anticipated LIEBIG in the announcement of what was afterwards called the law of the minimum. His statement regarding the effects of minimum and maximum factors on the growth of crops is as follows:—

"The value of a soil, whether surface soil or subsoil, can be ascertained to a certain extent from its physical appearance, from the quantity of its elutriable particles, from the character of the native plants and cultivated crops that grow upon it, and in other ways, but the only perfectly reliable method of determining its value is to subject it to a chemical analysis in order to determine whether it contains a sufficient amount of those substances that serve plants as food. The soil is often neither too stiff nor too porous, neither too wet nor too dry, neither too cold nor too warm, neither too high nor too low; it may be situated under very advantageous climatic conditions, it may contain a goodly proportion of elutriable particles, it may have an abundant supply of humus and be located on a favorably inclined slope and yet may often be unproductive because it is deficient in *one single element* that is necessary as a food for plants. Again it may also fail to bear good crops because it contains a very easily water-soluble plant food in too great an excess or because it contains substances that act as poisons to the growth of plants" (Bodenkunde, 1837, pp. 303-4).

In this, as in other passages, SPRENGEL not only indicated the numerous physical, chemical and climatic factors that contribute to soil productivity but he also stressed in unmistakable language the significance both of a deficient and of a superabundant plant nutrient.

Other similar statements regarding avoidance of a deficiency or excess are elaborations of a favorite doctrine of SPRENGEL's teacher, THAER. The elements supplied to crops must also be in the proper state, neither too soluble, nor too insoluble. The maintenance of a proper balance in the needs of crops for plant food, water, sunshine, etc., was especially emphasized by SPRENGEL. Seeds which are planted must also have the proper balance of components to support the growth of the plant embryo. Chemical analysis is the only means of determining whether the fertilizing constituents of soils, fertilizers, seeds, etc., are in proper proportion without too much or too little of any single ingredient. SPRENGEL was blamed by his critics for insisting too strongly upon the doctrine of avoiding "too much" or "too little", as this could be used as a subterfuge for explaining almost any theory (Dünger, 1845, p. 76).

SPRENGEL's method of determining soil deficiencies was to note the composition of the soil where a good crop was obtained and then to compare with this the analysis of a soil which produced an inferior crop. The following analyses are quoted from his tables of the composition of soils (Bodenkunde, 1844, pp. 514-6):—

	<i>A Very Productive Soil</i>	<i>A Very Unproductive Soil</i>
Silica and fine quartz sand.....	83.298 percent	88.088 percent
Alumina (combined with silica).....	1.413	2.624
Alumina (free and combined with humic acid)	3.715	1.254
Ferric and ferrous oxide (combined with silica)	0.724	1.740
Ferric and ferrous oxide (free and combined with humic acid).....	2.244	1.365
Manganic and a little manganous oxide	0.280	0.133
Lime (combined with carbonic, humic, sulfuric and phosphoric acids)...	1.824	0.149
		0.081
Magnesia (combined with silica)....	0.422	0.260
Magnesia (combined with humic acid)	0.400
Potash	0.003	trace
Soda	0.001	trace
Phosphoric acid	0.166	trace
Sulfuric acid	0.069	0.112
Chlorine	0.002	trace
Carbon dioxide (combined with lime)	0.440
Humic acid	0.789	0.720
Humus (with a little water).....	3.250	3.474
Nitrogenous substances	0.960	trace
Waxy resin	trace
	100.000	100.000

It will be noted in the above table that in the unproductive soil there is a deficiency of lime, potash, soda, phosphoric acid, chlorine and nitrogenous substances, ingredients to which SPRENGEL attached great significance in the nutrition of crops. The percentage of potash recorded for a productive soil is evidently much too low.

With regard to humus and humic acid the two soils show but little difference in composition. Other comparisons of a similar character and the observation that soils rich in humus might be unproductive and soils of low humus content might be highly productive led SPRENGEL to the conclusion that too much significance had been attached by earlier writers to the value of this constituent as a plant food. He admitted, however, that humic acid might play an important part in the maintenance of soil fertility by its solvent action in increasing the availability of the mineral constituents of the soil. In fact he attributed the fertilizing value of humus mainly to its content of these constituents such as potash, soda, lime, magnesia, sulfuric acid, phosphoric acid and chlorine. He held that humus containing much ferrous sulfate had a deleterious action on the growth of plants. The organic matter of humus was regarded by SPRENGEL as of little food value to plants. He remarked in this connection:—

“The conviction should have been reached long ago that humus is not such an important substance as we have been led to believe and that the current doctrine of humus is exceedingly full of contradictions. The old view, however, continues to be firmly retained, for we see daily how it has been copied from older into later works and even into the latest,—a circumstance of much convenience for agricultural writers but one that does not advance science or practice a single step. It is in fact most remarkable

that a doctrine, so senseless and false in its conclusions, should have been and should be so continually maintained and that it did not long ago collapse like a building on shaky foundations. The situation may be explained by considering first how erroneous are the present conceptions of plant nutrition and secondly how extremely defective were the experiments upon which the old doctrine was based. We are therefore not at all justified in continuing to maintain as uncontrovertible truth what has been asserted for the past 25 years. It would be superfluous for me to repeat what I have already written upon the subject in my "Chemistry" and "Treatise on Fertilizers". I will only state that I am more than ever convinced of the correctness of my previously expressed views and that, although regarding humus as a very important soil constituent, I have come more and more to the conviction that plants can entirely dispense with it" (Urbarmachungen, 1838, pp. 188-9).

We see in this passage as in so many others how SPRENGEL anticipated many of the views that were later expressed by LIEBIG. An analysis by SPRENGEL (1826*b*) of the organic matter of plant humus by combustion with cupric oxide indicated a carbon content of 58 percent and this value was used by WOLFF, VAN BEMMELEN and later investigators as a means of estimating humus in a method by which the organic carbon content of the soil was multiplied by the factor $\frac{100}{58}$ or 1.724.

SPRENGEL in his *Bodenkunde* divided soils, according to their physical and chemical characteristics, into the following main groups: (1) gravelly, (2) sandy, (3) loamy, (4) clayey, (5) calcareous, (6) marly, (7) humic, (8) peaty, (9) swampy, (10) talcose, (11) gypseous and (12) ferruginous. Soils combining the features of several groups were classified as sub-groups, such as sandy-clay, calcareous-loam, humus-marl, etc. The properties and adaptations of these various soils to different crops are discussed, methods for determining their chemical composition are fully described and the analyses of 180 soils from different parts of the world are tabulated with descriptions and comments. His analyses of two very fertile soils of the Ohio district have an interest in being among the earliest recorded complete analyses of American soils.

SPRENGEL concluded, as a result of his extensive determinations of the mineral constituents of soils and crops, that the quantities of these various elements in one and the same plant are always dependent upon the chemical composition of the soil on which the plant is grown. In this connection he remarked:—

"The different parts of plants contain their elementary constituents in widely varying proportions. The grain of wheat is much richer in phosphorus, sulfur, nitrogen, calcium, potassium, sodium and chlorine, while wheat straw contains only small amounts of these elements but much more of silicon. It follows therefore that if we wish to grow wheat with a high yield of grain, the soil, or its fertilizer, must be amply provided with the seven elements above named. Experience demonstrates that this is always actually the case.

"In seed grain which is perfectly developed we find all the elementary constituents, that are found afterwards in the entire plant. This is very important for the seed must first provide the developing germ with all those elements which the plant in its future growth afterwards obtains from the soil and air. If the seed grain does not contain the requisite amount of this or that element which is necessary for the complete development of the germ, or if any one element occurs in too great an excess, it cannot produce a perfect germ and an imperfect plant will be the natural consequence. Many soils have such a satisfactory mixture of ingredients, that they always produce seeds of the best chemical constitution, which is the true explanation why certain lands

have acquired so excellent a reputation for the high quality of their seed grain" (Dünger, 1845, p. 47).

SPRENGEL emphasized the fact that plants differ greatly in their preferences and requirements for the various mineral elements of the soil. Usually only slight amounts of these elements suffice for the growth of a plant.

"If, however, an element, necessary for the chemical constitution of this or that plant, is completely lacking in the soil or fertilizer, it is impossible for it to grow, for so far as we now know, no necessary element in the processes of vegetation can be replaced by another, or still less be generated by transmutation, although formerly there were many, and even now occasionally a few, who maintain this position. The experiments however, upon which such opinions are based, were very imperfectly performed." "It has recently been asserted that the bases lime, magnesia, potash and soda can replace one another. . . . I must, however, contradict this assertion. It is never possible for example to grow good buckwheat upon peaty soils by fertilizing them with lime. Excellent crops, however, are obtained by applications of wood ashes or potash" (*loc. cit.*, pp. 58-9).

SPRENGEL maintained that in addition to the soil elements which promoted the growth of plants, there were other elements, as lead, arsenic and selenium, which injured the growth of plants if they existed in combinations that were easily soluble in water. He stated, however, that all plants were not affected alike by these injurious elements, one species having a greater power of resistance than another. SPRENGEL seems to have been the earliest to call attention to the possible injurious effects of selenium upon the growth of plants.

One of the first definite expressions of the close relationship of soils to animal nutrition was made by SPRENGEL in the following significant passage: —

"Red clover for example which has grown upon a marly soil, always contains more calcium, phosphorus and sulfur than red clover which has grown upon a loamy soil since the latter as a rule does not make available to red clover as much calcium, phosphorus and sulfur as the marly soil. If we consider next that calcium, phosphorus and sulfur are most essential for the growth of the animal body, it is perfectly evident, as repeated experiments on a large scale have proved, why clover from a marly soil is more nutritious than clover from a loamy soil. . . ." (*loc. cit.*, p. 46).

In his "Lehre vom Dünger" SPRENGEL first describes the proximate constituents of plants and the chemical processes which govern their growth. The fermentation, decomposition and decay which take place in the composting of vegetable and animal substances are discussed as a general preliminary to a description of methods for the utilization by plants of agricultural wastes such as the excreta of animals, bones, tankage, straw, weeds, leaves and other plant materials.

According to SPRENGEL plants, through the agency of their leaves and roots, can eliminate injurious substances to a certain extent, the stronger plants in this respect excelling the weaker. SPRENGEL laid considerable stress upon the excretory function of the roots and held that the excreta of one plant may be injurious to another. Winter rye, if planted immediately after potatoes, does not do so well as summer rye. SPRENGEL suggests this may be due to a toxic exudate of the potato which is destroyed in the fallowing that precedes the later planting. Weeds may also injure

crops not only by the theft of plant food but by the exudation of toxic products through the roots. SPRENGEL suggests that organic acids produced by the decomposition of humus may have a toxic action upon plants, although he is inclined to doubt the existence of the hypothetical crenic, apocrenic and geic acids of BERZELIUS and his school. In his theory of toxic exudations by the roots of plants SPRENGEL follows a doctrine first suggested by BOERHAAVE and afterwards developed by DE CANDOLLE.

SPRENGEL classifies fertilizing materials into (1) the purely animal manures, as excreta, urine, guano, bones, blood, tankage, fish scraps, etc., (2) the purely vegetable manures, as straw, vines, weeds, leaves, etc., (3) the mixed animal and vegetable manures, as stable manure, (4) the green manures, i.e., green plants which are plowed under, (5) the mineral manures, as lime, marl, clay, loam, wood and plant ashes, sulfates of potash, soda, lime, iron, alumina and ammonia; chlorides of lime, alumina and soda; nitrates of potash, soda, lime and ammonia; carbonates of potash, soda and ammonia and (6) the mixed mineral and organic manures, such as the sediment of ponds and ditches and street sweepings. The properties of the various fertilizing materials are discussed and analytical methods for determining their manurial value are described.

In the final pages of his "Lehre vom Dünger" SPRENGEL discusses the value of the small percentages of fertilizing constituents contained in rain and irrigation water and the benefits of soaking seed grain in solutions of fertilizing compounds as a means of promoting germination.

SPRENGEL in his numerous publications in ERDMANN'S Journal gives many detailed analyses of the ashes of the grain, seeds, straw, vines, tubers, etc., of different crops and emphasizes the fact that the necessary constituents of these ashes, if lacking in the soil, must be supplied by fertilizers. In his review of this work LAMPADIUS (1832) made the following remark:—

"The readers of this Journal, who are interested in the application of chemistry to agriculture, are of course familiar with the views expressed in its previous volumes by Dr. SPRENGEL that the inorganic constituents which we find in plants are not accidental and unessential, but, being necessary for the existence of plants, are taken up from the soil, so that in compounding mineral fertilizers we must therefore take care to supply these constituents to the soil if they are lacking."

SPRENGEL was thus recognized long before LIEBIG as a proposer of the doctrine of mineral fertilizers. LIEBIG (1862), always jealous of his own claims for this discovery, disputed this recognition on the basis of the great inaccuracy of SPRENGEL'S analyses and also because he failed to distinguish between essential and unessential ash constituents. While this does not affect the priority of SPRENGEL'S announcement LIEBIG was perfectly correct in the main facts of his criticism. SPRENGEL'S analyses both of soils and of plant ashes are exceedingly faulty, as are most other similar analyses performed before 1850. The same criticism applies also to various incorrect analyses quoted by LIEBIG in the first 1840 edition of his book which he accepted at the time as valid. Upon the basis of faulty evidence LIEBIG (1840) asserted that the bases lime, magnesia, potash and soda were mutually replaceable as fertilizers—a statement to which SPRENGEL took strong exception (Dünger, 1845, p. 59). SPRENGEL undoubtedly

went too far in assuming that various constituents of his plant ashes, as alumina and soda, were essential to plant growth but exact information upon this point could not be gained until years later after the improvement of water culture methods.

Another error committed by SPRENGEL relates to his theory of nitrogen fixation by means of burnt clay. The improvement of soils by applications of burnt clay was advocated by many writers a century ago. SPRENGEL attributes the fertilizing action of such clay, which should be only gently roasted, to the presence of ferrous oxide. He supposed the latter on contact with water to withdraw oxygen and liberate hydrogen which on combination with the nitrogen of the air would produce ammonia. SPRENGEL (1830) reported the evolution of ammonia on heating burnt clay that had been exposed to the air.

Although SPRENGEL rejected THAER's opinions regarding the generation of mineral elements and the assimilation of humus by plants he accepted his vitalistic doctrines and expanded them to a fantastic extreme.

"What the nature of vitality is," he remarks, "we do not know but its presence and activity are indicated by the fact that it forces simple substances, contrary to their chemical affinity, to enter into, and remain in, combinations such as do not occur in inorganic nature and such as art is unable to produce." . . . "If the life of an organized body begins to disappear the chemical forces again become active and there arise then not only compounds such as occur in inorganic nature but also bodies in which a remnant of vital force is still noticeable. The latter, to which humic acid, urea, etc., belong can be regarded as transition products of the living into the non-living" (ERDMANN's Jour. 17: 185-6, 1833).

To the remnants, or atoms, of vital force clinging to humus, urea, etc., SPRENGEL attributed a peculiar generative and invigorating action. Organic manures are thus to be preferred to inorganic and organic medicines to inorganic. SPRENGEL regarded life as something resembling an indestructible chemical element: —

"The number of chemical elements which can combine with life is very few for they are the only ones that are met with in plants and animals. The greatest number of life atoms, if I may so express myself, are found in those organic substances that are composed of very many chemical elements; albumen composed of 8 or 9 elements will therefore have more life atoms than malic acid. A highly organized body is therefore composed of many life atoms and many chemical atoms. If the organic body contains too many life atoms, it is a poison. . . . In the decay of plants the life atoms enter into other combinations (for the chemical substances are always their carriers) but they do not distribute themselves among all the newly formed substances but only among a few. If, for example, humic acid, acetic acid, silica and iron oxide are formed then the first two receive the life atoms and the last two none. If the humic acid and acetic acid are in turn decomposed then the life atoms escape with the carbonic acid. . . . When carbonic acid is assimilated it is decomposed; the oxygen escapes unutilized and the life atoms that remain serve for vitalizing the substances absorbed by the roots. The inner nature of the life atoms is as little explainable as that of the chemical atoms" (ERDMANN's Jour. 7: 176-7, 1830).

Highly imaginative speculations of this character occurring in the midst of passages of sound scientific reasoning come as a shock to the modern reader. Undoubtedly SPRENGEL's almost medieval vitalistic conceptions served to discredit him in other matters where his opinions were far in advance of their time. By the end of the nineteenth century his writings

were rarely referred to and at the present time he might almost be called "the forgotten man of agricultural chemistry".* CARL SPRENGEL should always be remembered as one who paved the way for LIEBIG and as one whose chief aim was to make agricultural chemistry a practical science.

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— (1830): ERDMANN's Jour. für tech. und ökonom. Chem. 8: 215.

Jean-Baptiste (Joseph Dieudonné) Boussingault (1802-87):— Agricultural chemistry has been defined as that branch of applied science which treats of the chemical composition and mutual chemical relationships of soils, fertilizers, crops, and farm animals. Until the third decade of the nineteenth century agricultural chemists had occupied themselves chiefly with problems of chemical composition and very little with problems of mutual chemical relations. Much knowledge had been accumulated concerning the elementary composition of agricultural products but no one had yet attempted to follow the balance of chemical elements in the growing of a crop or in the feeding of an animal. The chemist who first made agricultural chemistry a true experimental science by transferring it from the laboratory to the field and stable was J. B. BOUSSINGAULT. As has been truly stated by Sir E. J. RUSSELL (1937), "to BOUSSINGAULT belongs the honor of having introduced the method by which the new agricultural science was to be developed".

BOUSSINGAULT was born in Paris and after his primary education obtained his general scientific and chemical training at the Mining School at Saint Étienne. He was a precocious youth and when little more than twenty years of age obtained a position as mining engineer in South America where he remained for over ten years. During this period he published many papers, upon the geology, mineralogy, meteorology, etc. of the Andean Cordilleras, in the *Annales de Chimie et de Physique* and collected a wealth of agricultural observations that were included in his later works on rural economy. On returning to France he taught chemistry for a short time at Lyons. Having acquired through his wife the interest in an estate at Bechelbronn in Alsace, he began upon this property a long, carefully planned series of field experiments on the changes in the

* As good a historian of chemistry as ERNST VON MEYER was so ignorant of CARL SPRENGEL's work that he confused him with KURT SPRENGEL the botanist (History of Chemistry, English translation 1891, p. 479).

elementary composition of seeds during germination, the assimilation of atmospheric nitrogen by plants, the rotation of crops, the use of fertilizers, the care of barnyard manure, the nutritive value of forage crops, the feeding of farm animals, the influence of rations on the yield and composition of milk, and many other subjects of practical agricultural importance. These experiments, which were coördinated with careful laboratory control, were described in a series of articles that BOUSSINGAULT published in the *Annales de Chimie et de Physique* for 1836 and succeeding years. The appearance of these contributions marked the beginning of a new era in agricultural chemical research.

BOUSSINGAULT's growing reputation led to his appointment in 1839 as professor of agricultural and analytical chemistry at the Conservatoire des Arts et Métiers in Paris, a position which he held for the remainder of his life. For a long period he spent half of each year at Paris in discharge of his professorial duties and the other half on his estate at Bechelbronn in the pursuit of his agricultural experiments.

In 1844 BOUSSINGAULT collaborated with J. B. DUMAS in the publication of a small volume entitled, "Essai de Statique Chimique des Êtres organisés", which was the amplification of a lecture, given by DUMAS on August 20, 1841, before his class at the School of Medicine, upon the mutual chemical relations of plant and animal life. The following outline of these relations was given (DUMAS, 1844a, p. xiii):—

Programme

<i>Animal</i>	<i>Plant</i>
A moving organism	A non-moving organism
An oxidizing organism	A reducing organism
Exhales carbon dioxide, water, ammonia, nitrogen	Fixes carbon dioxide, water, ammonia, nitrogen
Consumes oxygen; neutral nitrogen compounds; fats; starches, sugars, gums	Produces oxygen; neutral nitrogen compounds; fats; starches, sugar, gums
Produces heat	Absorbs heat
Produces electricity	Absorbs electricity
Restores its elements to the air or earth	Draws its elements from the air or earth
Transforms organic matters into inorganic	Transforms inorganic matters into organic

This scheme of the chemical relations of plant and animal life, as amplified in the text and notes of the "Essai de Statique" was the first compendium of its kind, and, although misleading and incomplete in the light of present knowledge, it served a useful purpose. The work became very popular and passed through three French editions. An English translation entitled, "The Chemical and Physiological Balance of Organic Nature" was published at London in 1844; the book was also translated into Dutch, German, Italian, and Spanish.

A blemish of the work was its over-insistence upon French priority. In this respect it was a counterblast to the exaggerated claim of LIEBIG, made in 1840 in the preface of his "Organic Chemistry in its Applications to Agriculture and Physiology" that until he took up the subject no chemist since the time of DAVY had occupied himself in studying the applications

of chemistry to plant and animal life. DUMAS' answer to this challenge is thus expressed at the close of the third edition (Paris, 1844) of his book (p. 140) :—

"We are convinced that, if the views proposed in this lecture retain in the future the same importance that is accorded them today, it will continue to be shown that the principal researches, on which these views are based, were carried out in France and that their comprehension into one general formula is due to LAVOISIER who gave to physiology the impulse which we have followed. If we are not mistaken, this will easily continue to be shown. Otherwise it must be proved that we have been wrong in attributing

(1) to LAVOISIER, the discovery of the theory of animal heat and of the oxidizing rôle that characterizes animals; also the first application of the balance to vital phenomena.

(2) to SENEBIER, the discovery of the decomposition of carbonic acid by plants.

(3) to BOUSSINGAULT, the discovery of the decomposition of water by plants and the use of the balance in studying the phenomena of plant growth.

(4) to SCHATTENMANN and to DAVY, the discovery of the rôle of ammonia in vegetation.

(5) to BRONGNIART and PARROT, the first idea of attributing to atmospheric carbonic acid the source of all the carbon of living things.

(6) to VAUQUELIN, BOUSSINGAULT, MULDER, PROUST, and BRACONNOT, the discovery of fibrine, albumin, and casein in plants.

(7) to DUMAS and BOUSSINGAULT, the discovery of the general reducing rôle of the vegetable kingdom.

(8) to CHEVREUL, the discovery of the true theory of animal respiration."

This tabulation, important and truthful as it may have seemed to DUMAS at the time, has lost its significance. Several of the names proposed have been forgotten, some of the claims have lost importance and all of them require qualification.

In 1843-4 BOUSSINGAULT assembled his scattered articles on agricultural chemistry and related subjects and published them with much additional material in a two-volume work entitled, "*Économie Rurale, considérée dans ses rapports avec la chimie, la physique et la météorologie*". The book had an extensive demand and passed through several editions and translations. The second revised French edition was published at Paris in 1851. An English translation, "Rural Economy in its relations with Chemistry, Physics and Meteorology; or Chemistry applied to Agriculture" by GEORGE LAW, with an introduction and notes, was published in New York and Philadelphia in 1845. A German translation by GRAEGER was published at Halle in 1844. The second edition of the German translation, published in 1851, was supplemented in 1854 by a third volume containing the revisions of the second French edition, and in 1856 by a fourth volume of other additions. An Italian abstract was published at Vercelli in 1845 and a complete Italian translation with notes by JAC. BOLOGNA was printed at Venice in 1850. It will be noted that BOUSSINGAULT avoided the title "Agricultural Chemistry" as the sole designation of a field where several sciences are involved. He was meticulously careful to limit the expression "Agricultural Chemistry" to purely chemical matters. It is to the first French edition of the "*Économie Rurale*" that the following translations and references pertain.

The general scope and plan of BOUSSINGAULT's "*Économie Rurale*" are indicated by the following paragraph from his preface :—

"The first part of this work treats in succession of the physical and chemical phenomena of plant growth; of the composition of plants and their immediate principles; of fermentation; and of soils. The second part gives a résumé of the investigations that have been made upon fertilizers and soil amendments; a discussion of the relative value of crop rotations; general remarks on stockfeeding and animal husbandry; and finally some consideration on climatology and on the relations between living beings and the atmosphere" (p. viii).

Only a few of the more striking features of BOUSSINGAULT's researches will be considered.

Elementary Losses during Germination of Seeds.—DE SAUSSURE (1804a) had shown that seeds require oxygen in order to germinate and that during germination the amount of carbon dioxide evolved is in general approximately equal to that of the oxygen absorbed. Certain exceptions to this rule were later found by DE SAUSSURE, the volume of an enclosed atmosphere during germination being found in some cases to diminish and in others to increase. Utilization of atmospheric oxygen to form organic acids or to oxidize the hydrogen of fats to water would cause a lowering in the ratio of carbonic acid to consumed oxygen; auto-oxidation of the seed substance, through combination of its own carbon and oxygen, might cause on the other hand more carbonic acid to be evolved than the equivalent of oxygen consumed from the air. It was to throw more light upon these uncertainties that BOUSSINGAULT made the first investigation upon elementary losses during germination.

In the following experiment the total dry substance and elementary analysis of clover seed on an ash-free basis was determined before and after germination. A calculation of the weights of elementary components in the dried seed at the beginning, as determined by analyses of similar seeds from the same lot, and in the dried germinated seeds at the end of the experiment, indicated the following losses (Vol. 1, p. 39):—

Table 1.—CHANGE IN COMPOSITION OF CLOVER SEEDS DURING GERMINATION

	Total weight	Carbon	Hydrogen	Oxygen	Nitrogen
Clover seeds, ungerminated...percent		50.8	6.0	36.0	7.2
Clover seeds, germinated....percent		51.5	6.3	34.2	8.0
Clover seeds, ungerminated...grams	2.405	1.222	0.144	0.866	0.173
Clover seeds, germinated....grams	2.241	1.154	0.141	0.767	0.179
Difference	—0.164	—0.068	—0.003	—0.099	+0.006

The results indicate a distinct loss of oxygen in the seeds during germination. This loss, however, is only a little more than the calculated amount (0.091 gm) necessary to unite with the loss in carbon (0.068 gm) to form carbon monoxide. To complete the oxidation to carbon dioxide, one volume of atmospheric oxygen would be used for every two volumes of carbon dioxide produced, so that in this germination experiment there was a gain in the volume of the surrounding air which BOUSSINGAULT calculated to be about 64 cc.

BOUSSINGAULT pointed out that as soon as the young plantlet develops chlorophyll and begins to assimilate carbon dioxide, the process becomes vastly more complex.

"This action of the green matter becomes apparent long before the primary phase of germination has entirely ceased, so that during a certain time two opposite forces are simultaneously at work. One of these, as has been shown, tends to eliminate carbon from the seed; the other tends to supply it. So long as the first of these forces predominates the seed loses carbon; but with the first appearance of its green tissues the young plant recovers a part of it; finally, when by progressive vegetation the second force surpasses the first in intensity, the plant gains and advances rapidly to maturity" (Vol. 1, p. 42).

The field which BOUSSINGAULT opened by these experiments was developed later along similar lines by HELLRIEGEL, SACHSSE and other investigators. The problem of the elementary changes in the germination of seeds is still a subject of investigation.

Assimilation of Atmospheric Nitrogen by Legumes.—The sources from which crops derive their nitrogen had long been a puzzle to agricultural chemists. It was known to the ancient classic writers on agriculture that the ploughing under of certain leguminous crops enriched the soil. Thus PLINY in his Natural History (Book 18, Chap. 30) mentions that beans fertilize the ground in which they have been sown as well as any manure. With the improvements in methods for analyzing agricultural products, which began in the early nineteenth century, it was realized that the leguminous crops were highly nitrogenous and suspicions were aroused that this family of plants might have a special capacity for fixing atmospheric nitrogen. In order to determine whether this was, or was not, the case, BOUSSINGAULT (1838) made use of his method of elementary analysis. He thus describes his plan of investigation:—

"I had necessarily to follow a method of inquiry different from any that had yet been taken; I had no likelihood of obtaining results more decisive than those previously found had I chosen the same means of investigation. I therefore called in the aid of elementary analysis, with a view of comparing the composition of the seed with the composition of the crop produced therefrom at the sole cost of water and air. By proceeding in this way I believed that the problem was capable of solution, although I do not flatter myself at all that I have completely solved it. The subject moreover is one of the most delicate imaginable and demands a certain amount of indulgence.

"I took as a soil baked clay, or siliceous sand, freed of organic matter by proper calcination. In this soil, moistened with distilled water, were sown the seeds whose weight had been determined. In a series of preliminary analyses I determined the moisture which seeds of the same kind, origin and time of sampling lost by drying first in an oven and then in an oil bath at 110°. The porcelain dishes, which contained the sandy soil, were placed in a glass house at the end of a large garden. During the whole time of growth, the windows were hermetically closed, but their situation permitted free access of sunshine during the whole day. To harvest the crop, the dishes were first dried at a gentle heat. The roots of the plants then came out readily; to free them completely from adhering sand, they were moved about in distilled water but never crushed for fear of losing some of their juice. It seemed preferable even to leave a little sand adhering. The harvested plant was then dried in the oven so that it could be powdered; final desiccation was accomplished in an oil bath in vacuo.

"A determination by combustion of the weight of ash, enabled a calculation to be made of the weight of crop free from all saline and earthy matter. Elementary analysis then indicated the composition of the crop. All that was now left was to compare this with the composition of the seed in order to know the proportion and nature of the elements which had been assimilated during growth" (Vol. 1, pp. 71-3).

The following results were obtained in growth experiments with clover, peas, wheat and oats (Vol. 1, pp. 74-82):—

Table 2.—EXPERIMENTS SHOWING ASSIMILATION OF ATMOSPHERIC NITROGEN BY CLOVER AND PEAS

	Weight, ash-free Substance grams	Carbon grams	Hydrogen grams	Oxygen grams	Nitrogen grams
Red clover, seed	1.586	0.806	0.095	0.571	0.114
Red clover, crop, 3 months....	4.106	2.082	0.271	1.597	0.156
Gain	2.520	1.276	0.176	1.026	0.042
Peas, seed	1.072	0.515	0.069	0.442	0.046
Peas, crop, 3 months.....	4.441	2.376	0.284	1.680	0.101
Gain	3.369	1.861	0.215	1.238	0.055
Wheat, seed	1.644	0.767	0.095	0.725	0.057
Wheat, crop, 2 months.....	3.022	1.456	0.173	1.333	0.060
Gain	1.378	0.689	0.078	0.608	0.003
Oats, transplanted seedling		0.827	0.106	0.568	0.059
Oats, crop, 41 days.....		1.500	0.193	1.372	0.053
Difference		+0.673	+0.087	+0.804	—0.006

The following summary of these experiments was made by BOUSSINGAULT:—

"(1) That clover and peas, grown in a soil with absolutely no fertilizer, gained, in addition to carbon, hydrogen and oxygen, an appreciable quantity of nitrogen.

"(2) That wheat and oats, grown under the same conditions, also took carbon, hydrogen and oxygen from the air and water but that analyses could detect no gain in nitrogen after the growth of these cereals.

"The purpose of this method of investigation was simply to establish the fact of nitrogen assimilation by certain plants, without entering into the question of the means by which this was effected, and upon this point I can only offer conjectures" (Vol. 1, pp. 82-3).

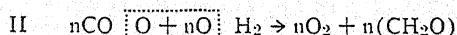
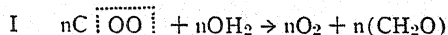
The mechanism of the fixation of atmospheric nitrogen by legumes remained an unsolved mystery for the next half century until it was finally explained in 1886 by HELLRIEGEL and WILFARTH who localized the nitrogen fixing organs of the plant in the root nodules.

Fixation of the Hydrogen of Water by Plants.—When the improving art of chemical analysis showed that the ratio of hydrogen to oxygen in sugar, starch, cellulose and other carbohydrate materials was exactly the same as that existing in water, the mechanism of the photosynthetic process was naturally assumed to be a simple combination of carbon atoms from the assimilated carbon dioxide with water molecules from the soil solution. The production by the plant of substances that contain an excess or a deficiency of hydrogen or oxygen was then attributed to an addition or withdrawal of these elements from the parent carbohydrate molecule. The exact manner in which water was fixed or decomposed in these elementary transmutations was not, however, indicated.

That water participated in the assimilation process was first suggested by SENEBIER. Later DE SAUSSURE (1804b) showed that the two processes

of assimilation of carbon and fixation of water were inextricably associated, there being no increase in weight of a plant in a carbon dioxide-free atmosphere; when, however, carbon dioxide was present there was an increase in weight in excess of the amount of carbon assimilated which could only be explained upon the basis of a simultaneous fixation of water.

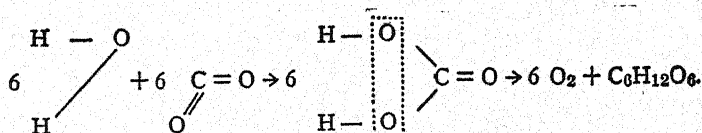
BOUSSINGAULT's elementary analyses of clover, peas and other seedlings indicated to him that there was not only a fixation but a decomposition of water in the assimilative process. His results showed usually an excess of hydrogen above that needed to combine with the oxygen to form water—an observation which suggested to him the possibility that water and carbon dioxide might undergo simultaneous decompositions in the photosynthetic process with fixation of carbon, hydrogen and oxygen by the plant and liberation of oxygen. The two photosynthetic processes, according to scheme (I) of having all the evolved oxygen come from the carbon dioxide and according to BOUSSINGAULT's scheme (II) of having it come from both the carbon dioxide and water, may be represented by the following equations:—



In explaining his scheme of water decomposition by plants BOUSSINGAULT remarked as follows:—

"In the hypothesis that we are discussing, for each volume of carbonic acid modified during vegetation a half volume of oxygen will be liberated. The oxygen in excess of this half-volume, must be regarded as coming from decomposed water, the hydrogen of which will have been assimilated by the plant at the same time as the carbon monoxide derived from the carbonic acid" (Vol. 1, p. 87).

According to the present-day assumption that carbon dioxide is not decomposed directly but only after its appearance in the water of the cell solution as carbonic acid (H_2CO_3), the evolution of oxygen in the photosynthetic process would take place equally, as suggested by BOUSSINGAULT, from the original two reacting molecules. Thus



water + carbon dioxide \rightarrow carbonic acid \rightarrow oxygen + sugar

Carbon dioxide assimilation interested BOUSSINGAULT for over forty years after the publication of his first researches on the subject. In a later very exhaustive article BOUSSINGAULT (1864) reported 41 determinations of the balance between absorption of carbon dioxide and evolution of oxygen by the leaves of 25 different plants. The average of these determinations indicated that for 100 vols. of carbon dioxide assimilated there were 98.74 vols. of oxygen and 1.21 vols. nitrogen exhaled.

Soil Chemistry.—Chapter IV of the "Economie Rurale" is devoted to Soils. BOUSSINGAULT did not share the confidence of SPRENGEL and other writers as to the value of soil analysis.

"Much has been written," he remarks, "since BERGMAN's time on the chemical composition of soils. Chemists of the highest rank have made complete analyses of soils that were noted for their high fertility. Nevertheless practical agriculture has derived hitherto only a very meagre benefit from labors of this kind. The reason of this is very simple; the qualities that we value in tillable soils depend almost exclusively upon the mechanical mixture of its different aggregates and not upon their chemical composition. A simple elutriation, which indicates the proportion of sand to clay, tells us vastly more than a detailed analysis" (Vol. 1, pp. 563-4).

With regard to the conflicting schools of opinion concerning the nutritive value of humus BOUSSINGAULT took an intermediate position.

"It is probable," he remarks, "that both parties have advanced extreme opinions. Plants probably draw from the atmosphere more than agriculturalists generally suppose and the soil furnishes to plants, independently of saline and earthy substances, a proportion of organic matter greater than certain physiologists imagine" (Vol. 2, p. 259).

It was on the nitrogenous matter of humus that BOUSSINGAULT laid chief stress and he was one of the first to emphasize the importance of determining the nitrogen in the organic matter of the soil (Vol. I, p. 571).

BOUSSINGAULT recognized the importance of making ash analyses of crops for the purpose of determining the depletion of necessary mineral elements from the soil, but stressed the fact that comparisons to be profitable should be made

"on the analysis of the ashes of plants grown in the same soil and manured with the same fertilizer of which the content in mineral substances was known. A kind of current account should be established between the inorganic matter of the crop and that of the fertilizer" (Vol. 2, p. 323).

The following mineral balance of this kind was reported for a five-year rotation on his farm at Bechelbronn (Vol. 2, p. 336).

Table 3.—KILOGRAMS OF MINERAL CONSTITUENTS REMOVED PER HECTARE OF LAND

<i>Crop rotation</i>	<i>Total ash</i>	<i>Phosphoric acid</i>	<i>Sulfuric acid</i>	<i>Chlorine</i>	<i>Lime</i>	<i>Magnesia</i>	<i>Potash and soda</i>	<i>Silica</i>
1st year, potatoes.....	123.4	13.9	8.8	3.3	2.2	6.7	63.5	6.9
2nd and 4th years, wheat	55.0	25.8	0.6	...	1.6	8.8	16.2	0.8
2nd and 4th years, wheat straw	390.6	12.0	4.0	2.4	33.2	19.6	37.2	264.0
3rd year, clover.....	310.2	19.5	7.7	8.1	76.3	19.5	84.1	16.4
5th year, oats.....	42.6	6.4	0.4	0.2	1.6	3.3	5.5	22.7
5th year, oat straw.....	65.4	1.9	2.7	3.0	5.4	1.8	18.9	26.2
5th year, turnips	54.4	3.3	5.9	1.6	5.9	2.3	20.6	3.5
Mineral matter of crops.		82.8	30.1	18.6	126.2	62.0	246.0	340.5
Mineral matter of fertilizers		98.0	332.0	35.0	581.0	148.0	370.0	5508.0
Excess mineral matter in fertilizer		15.2	301.9	16.4	454.8	86.0	124.0	5167.5

Fertilizer Studies:—BOUSSINGAULT devoted much study to the influence of mineral fertilizers upon the yield and composition of crops. He remarked in this connection:—

"Practice anticipated science in the application of mineral fertilizers. If their useful effect cannot be denied, if the circumstances in which it is advantageous to use them and the conditions and quantities in which they should be applied to the soil have been the subject of long careful observation by farmers, it must yet be admitted that we are still far from understanding exactly how they act. This is another reason why we should persevere in studying their effects" (Vol. 2, p. 158).

Of BOUSSINGAULT's numerous experiments upon the effects of fertilizers, his results on the much discussed application of gypsum are selected as typical of his method. The yield of clover obtained at Bechelbronn on gypsum treated land was 5000 kg dry hay per hectare and on untreated land 1100 kg. The ash of the clover on the two soils showed the following composition (Vol. 2, pp. 225-7):

Table 4.—PERCENTAGE COMPOSITION OF THE ASH OF CLOVER

Ash constituent	Ash of good clover crop 1841		Ash of poor clover crop 1842	
	Grown without gypsum	Grown with gypsum	Grown without gypsum	Grown with gypsum
	Percent	Percent	Percent	Percent
Chlorine	4.1	3.8	3.3	3.0
Phosphoric acid	9.7	9.0	7.1	8.2
Sulfuric acid	3.9	3.4	3.1	3.2
Lime	28.5	29.4	33.2	36.7
Magnesia	7.6	6.7	7.3	10.2
Oxides of iron, manganese and aluminum	1.2	1.0	.6	traces
Potash	23.6	35.4	29.4	34.7
Soda	1.2	.9	2.9	.3
Silica	20.2	10.4	13.1	3.7
Total	100.0	100.0	100.0	100.0
Ash in dry crop	10.3	5.4	8.8	5.6
Ash per hectare, kilograms	113	270	97	280

Gypsum application has caused a perceptible decrease in the percentage of ash in the clover but on the other hand a marked increase in the total weight of ash constituents removed per hectare. The amount of each ash constituent removed is indicated in the following table (Vol. 2, p. 227):—

Table 5.—WEIGHT OF MINERAL SUBSTANCES CONTAINED IN CLOVER PER HECTARE

	Phos- Chlo- rine	phos- phoric acid	Sul- furic acid	Lime	Oxides Mag- nesia	of Fe, Mn, Al	Potash	Soda	Silica
	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.
1841									
Crop without gypsum	4.6	11.0	4.4	32.2	8.6	1.4	26.7	1.4	22.7
Crop with gypsum ..	10.3	24.2	9.2	79.4	18.1	2.7	95.6	2.4	28.1
1842									
Crop without gypsum	3.0	7.0	3.0	32.2	7.1	.6	28.6	2.8	12.7
Crop with gypsum ..	8.4	22.9	9.0	102.8	28.5		97.2	.8	10.4

The fertilization of clover with gypsum in these experiments increases the depletion of chlorine, phosphorus, sulfur, calcium, magnesium and potash on a given area over two fold.

BOUSSINGAULT criticized the root exudation theory of DE CANDOLLE on the ground (1) that his own experiments gave no evidence of such excretions and (2) that wheat, maize, potatoes and many other crops had been grown upon the same soil for many years in succession without evidence of injury (Vol. 2, pp. 268-71).

Nutritive Equivalents.— One of BOUSSINGAULT's earliest experiments at Bechelbronn related to the nitrogen content and nutritive equivalents of different forage crops. He based the nutritive value of crops upon their content of nitrogen—the essential element of vegetable albumen or gluten. Employing the method of DUMAS for determining nitrogen and taking the nitrogen content (1.15%) of ordinary air-dry hay as his basis the theoretical nutritive equivalent (E) of any forage crop as determined from its nitrogen content (n) would be $E = \frac{1.15 \times 100}{n}$. A number of BOUSSINGAULT's theoretical equivalents, as thus calculated and as compared with practical equivalents according to feeding experiments by BLOCK, PETRI, and THAER, are given in the following table (Vol. 2, pp. 438-9).

Table 6.—NUTRITIVE EQUIVALETS OF DIFFERENT FORAGE CROPS (BOUSSINGAULT)

Forage crop	Water	Nitrogen in dry substance	n Nitrogen in original substance	Theoretical nutritive equivalent 115/n	Nutritive equivalent by experiment		
					BLOCK	PETRI	THAER
	Percent	Percent	Percent				
Ordinary meadow hay	11.0	1.34	1.15	100	100	100	100
Red clover, 2nd year, cut in flower.....	10.1	1.70	1.54	75	100	90	90
New wheat straw, crop 1841	26.0	.36	.27	426	200	360	450
New rye straw.....	18.7	.30	.24	479	200	500	666
Oat straw	21.0	.36	.30	383	200	200	190
Pea straw	8.5	1.95	1.79	64	165	200	130
Cabbage	92.3	3.70	.28	411	556	500	429
Turnips	92.5	1.70	.13	885	533	600	526
Field beets, crop 1838	87.8	1.70	.21	548	366	400	460
Carrots	87.6	2.40	.30	382	366	250	300
Potatoes, crop 1838..	75.9	1.50	.36	319	216	200	200
Vetches in seed.....	14.6	5.13	4.37	26	30	54	66
Field beans	7.9	5.50	5.11	23	30	54	73
Yellow peas, dry....	8.6	4.20	3.84	27	30	54	66
Barley, crop 1836....	13.2	2.02	1.76	65	33	61	76
Wheat, crop 1836...	10.5	2.33	2.09	55	27	52	64
Rye, crop 1838.....	11.5	1.70	1.50	77	33	55	71

Metabolism Experiments.— BOUSSINGAULT applied his method of elementary balances also to the feeding of farm animals and the experiments which he conducted at Bechelbronn on this subject in 1839, in the words of LUSK (1922), "may be considered to be prophetic of the future evolution

of metabolism studies". In the introduction to his essay, "Comparative Analyses of the Food and Excreta of a Milch Cow; Investigations undertaken for the purpose of ascertaining if herbivorous animals assimilate nitrogen from the Air", BOUSSINGAULT (1839) made the following statement:—

"It is generally recognized today that the ration of animals should contain a certain amount of nitrogenous food. The presence of nitrogen in a large number of vegetable foods leads to the conclusion that herbivora derive from their food the nitrogen that enters into their constitution.

"In ordinary alimentation the individual does not change his average weight: this is always the condition when an adult animal is placed on a *maintenance ration*. It has been determined, for example, that a man who eats regularly regains his normal weight at certain times each day. Farmers know very well that by means of a carefully calculated ration they can give a horse the energy necessary for his required work without causing the animal to increase in weight.

"In such circumstances it is almost certain that the elementary constituents of the food consumed will be entirely recovered in the excreta, secretions and products of respiration. Under this consideration nitrogen is not assimilated any more than any of the other elements, if we understand by assimilation the addition of principles introduced by the food to principles already existing in the system. But there is evidently assimilation in the sense that the elements of the food enter the organism and after modification are fixed there in order to replace those that are daily expelled by the vital forces."

The elementary balance of carbon, hydrogen, oxygen, and nitrogen, excluding the products of respiration and transpiration, in BOUSSINGAULT's metabolism experiment are thus summarized:—

Table 7.—COMPOSITION OF RATIONS CONSUMED BY COW IN 24 HOURS

Ration	Original weight Grams	Weight of dry matter Grams	Carbon Grams	Hydrogen Grams	Oxygen Grams	Nitrogen Grams	Salts and minerals Grams
Potatoes	15000	4170	1839.0	241.9	1830.6	50.0	208.5
Rowen	7500	6315	2974.4	353.6	2204.0	151.5	631.5
Water	60000	50.0
A—Total ...	82500	10485	4813.4	595.5	4034.6	201.5	889.0

COMPOSITIONS OF EXCRETA, URINE AND MILK OF COW IN 24 HOURS

Excreta	28413	4000.0	1712.0	208.0	1508.0	92.0	480.0
Urine	8200	960.8	261.4	25.0	253.7	36.5	384.2
Milk	8539	1150.6	628.2	99.0	321.0	46.0	56.4
B—Total ...	45152	6111.4	2601.6	332.0	2082.7	174.5	920.6
Difference, A-B. +	37348	+4373.6	+2211.8	+263.5	+1951.9	+27.0	-31.6

In commenting upon these results BOUSSINGAULT attributed the differences in carbon to the exhalation of carbon dioxide and the differences in hydrogen and oxygen to the transpiration of water. The small difference in the nitrogen balance confirmed the view that this element is not assimilated from the air during animal respiration.

Composting Experiments.—Composting and the care of barnyard manure were subjects to which BOUSSINGAULT also applied his methods of organic analysis. He especially emphasized the effect of ration on the composition of the dung of animals. His compilation of the elementary

composition of the excreta of the horses, cows, and pigs of his Bechelbronn estate during one day is cited (Vol. 2, p. 77).

Table 8.—ELEMENTARY COMPOSITION OF THE DUNG OF FARM ANIMALS

Combined excreta in 24 hours from	Weight in dry state	Weight in wet state	Elementary composition of dry matter					Water in wet manure
			Carbon	Hydrogen	Oxygen	Nitrogen	Salts and minerals	
	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.	Kgs.
30 horses	111.4	467.4	43.0	5.6	40.5	3.0	19.3	356.0
30 horned cattle..	148.8	1098.4	59.2	7.0	52.8	3.9	25.9	949.6
16 pigs	12.0	66.7	4.6	.6	3.9	.4	2.5	54.7
Straw of bedding.	133.0	180.0	64.4	7.1	51.7	.5	9.3	47.0
Total	405.2	1812.5	171.2	20.3	148.9	7.8	57.0	1407.3

In commenting upon these results BOUSSINGAULT remarked: —

"Nitrogen is the element of highest importance which it is necessary to increase and conserve in manure. The organic substances that are most advantageous for producing fertilizers are precisely those which give birth, by their decomposition, to the largest amount of nitrogenous bodies whether soluble or volatile. I say by their decomposition for the mere presence of nitrogen in a substance of organic origin is not sufficient to make it a fertilizer. . . . But while admitting the importance, the absolute necessity even, of nitrogenous principles in fertilizers, we should not conclude that these principles are the only ones that contribute to fertilize the soil.

"It is beyond question that the alkaline and earthy salts are indispensable to the growth of plants and it is far from having been sufficiently shown that the non-nitrogenous organic principles of fertilizers play an entirely passive rôle. But with few exceptions the fixed salts, water or its elements, and carbon superabound in manure. The element existing there in smallest amount is nitrogen and it is moreover the one that is lost most easily during the alteration of the bodies that contain it. For these reasons it is actually the principle whose presence is of most importance to determine; its proportion establishes the comparative value of different manures" (Vol. 2, pp. 80-1).

For protecting barnyard manure against losses of nitrogen BOUSSINGAULT recommended close packing of the compost heap in order to prevent the aeration which is conducive to heating and sometimes to spontaneous ignition. He also spoke favorably of SCHATTENMANN's process of adding powdered sulfate of iron or of calcium to the manure pile in order to fix the ammonia and prevent its loss by volatilization (Vol. 2, p. 56).

Agricultural Chemical Economics.—The balanced economy of crop and animal production, which is generally recognized as the most perfect self-contained system of agriculture, received much attention from BOUSSINGAULT and is discussed by him at some length in Chapter IX of his book. His basic rule for farm management is: —

"That in no case is it possible to export from an estate more organic matter and particularly more organic nitrogenous matter than is represented by the excess of such matter in the manure applied in the course of the rotation. By acting otherwise the normal fertility of the soil would inevitably be diminished" (Vol. 2, pp. 501-2).

The statement is faulty in that BOUSSINGAULT laid too much stress upon organic matter and none at all upon essential mineral components. Obviously the exportation of organic matter from an estate in the form of

sugar, starch, cellulose or vegetable oils involves no depletion of soil fertility, since the elements of their composition are derived wholly from air and water. What BOUSSINGAULT had particularly in mind, however, was raw produce such as grain, hay, vegetables and other nitrogenous-containing produce. He was particularly concerned about the exportation of concentrates of high nutritive or manurial value.

"While it is wise," he remarks, "to encourage exportation, I also hold that there are substances for which it is prudent to discourage it; oil-cake, that powerful agent of fertility, can be placed in the first rank of these. In such cases I am far from sharing those principles of economists that are often too absolute. In my opinion any exportation, of which the consequence is an impoverishment of the soil, ought to be prohibited. I would oppose for example the exportation of arable soil; well then, to allow an active fertilizer to pass into the hands of strangers is in my eyes tantamount to exporting the vegetal earth of our fields, to lessening their productivity, to increasing the cost of living of the poor; for as much work, care and capital are required to produce little upon an ungrateful soil, as to produce much upon a fertile one" (Vol. 2, pp. 151-2).

This statement of BOUSSINGAULT represents the position of extreme agricultural self-sufficiency, whether local or general. It might be passed over as the relic of an outgrown system of philosophy, were it not for the fact that the economic doctrine of national self-containment is now being more rigidly enforced in many countries than ever before. It is a question after all of a balanced exchange. The farmer who sells his oil cake to a cattle feeder and buys back the manure has not only not impoverished his land but by stimulating trade has improved economic conditions. The same argument amplified applies also to states and to nations.*

BOUSSINGAULT's discussions of the utilization of agricultural products for the manufacture of starch, sugar, wine, oil, indigo, essential oils, resin, etc., are limited to brief descriptions of such technological operations as would ordinarily be conducted upon an estate. The industrial utilization of farm produce for the manufacture of paper, leather, soap, etc., falls outside the scope of his treatment.

The first nine chapters of BOUSSINGAULT's "*Économie Rurale*" gives one of the best coördinated accounts of the chemistry of farm operations that has ever been written. The concluding tenth chapter, on "Meteorological Considerations" discusses influences of temperature, rainfall, altitude and other climatic factors upon the growth of crops—topics that are more ecological than chemical. The simple courteous style of BOUSSINGAULT's book, coupled with its wealth of highly practical research material, makes it one of the great classics of agricultural literature.

In 1848, after the fall of LOUIS PHILIPPE, BOUSSINGAULT was elected to the National Assembly and shortly afterwards to the State Council, but in 1852 after the coup d'état of NAPOLEON III, he forsook politics and devoted the remainder of his life to the work of his professorship at the Conservatoire and to agricultural chemical research. His later investigations with those of various collaborators were published in a series of seven volumes entitled "*Agronomie, Chimie Agricole et Physiologie*" which appeared at irregular intervals between 1860 and 1884. These collected papers re-

* A severe criticism of BOUSSINGAULT's argument is contained in a footnote of LAW's English translation of the *Économie Rurale*, p. 300.

late to soils, fertilizers, plant physiology, animal nutrition, fermentation, storage of crops, methods of analysis and a large variety of other agricultural chemical subjects, the consideration of which falls beyond the scope of the present volume.

BOUSSINGAULT, who had experienced the deleterious effect of politics by the temporary loss of his professorship of agricultural chemistry at Paris in 1851, encountered heavier disappointments in another direction when his experimental farm at Bechelbronn became German territory in 1871 as a result of the conquest of Alsace in the Franco-Prussian War.

BOUSSINGAULT, LIEBIG, and MULDER were close contemporaries, and each was a founder of an important school of agricultural chemical research. In general agricultural significance the work of BOUSSINGAULT was by far the most important; his writings, because of their even calmness of tone and absence of personal antagonisms, were not so conducive to publicity as the more sensational contributions of LIEBIG. BOUSSINGAULT, who lived to a serene old age, had the satisfaction of seeing the principles of his work adopted in all parts of the world.

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— (1804b): *ibid.*, p. 220.

Gerardus Johannes Mulder (1802-80):— A school of agricultural chemistry, contemporary with those of BOUSSINGAULT and LIEBIG, was that of G. J. MULDER, Professor of Chemistry at the University of Utrecht. A large number of distinguished agricultural chemists obtained their training

under MULDER; among them was JOHN PITKIN NORTON, the first Professor of Agricultural Chemistry at Yale University.

MULDER was born at Utrecht, the Netherlands, at the University of which he obtained his degree of doctor of medicine in 1825. He began the practice of medicine in Amsterdam but was soon invited to teach botany and afterwards chemistry at the medical college of Rotterdam. In 1840 he was elected professor of chemistry at the University of Utrecht and retained this position until 1867 when he retired from active service.

MULDER's contributions to agricultural chemistry are contained chiefly in his "Proeve eener algemeene physiologische scheikunde" (Proof of a General Physiological Chemistry) which was published in two volumes at Rotterdam in 1844-46. A German translation "Versuch einer allgemeinen physiologischen Chemie" by MOLESCHOTT was published at Heidelberg in 1844-47. Another German translation was published at Brunswick in 1844-51. An English translation entitled, "The Chemistry of Vegetable and Animal Physiology" by P. F. H. FROMBERG, with introduction and notes by JAMES F. W. JOHNSTON, was published in successive parts at Edinburgh in 1845-49. It is to the latter work that the following page references (unless otherwise stated) pertain.

MULDER's "Proof of a General Physiological Chemistry" is in the main a treatise upon plant physiology. The modern chemist from his vantage ground of later acquisitions of knowledge finds in MULDER's book, as in the works of LIEBIG, a vast number of mistakes and erroneous speculations. Both men groped earnestly in the darkness for the light of truth. MULDER, however, lacked the ability of LIEBIG to subject his hastily published conjectures to rigid chemical tests. LIEBIG omitted from later editions of his books many of his earlier mistakes and by constant revision created a work of lasting memory. MULDER's books on the other hand are now rarely referred to and his name is mostly recalled in connection with the unfortunate controversies in which he became involved with LIEBIG. It was a "Sturm und Drang" period when, to quote Professor JAMES F. W. JOHNSTON, "An unnatural, and in some respects unworthy, excitement found its way into the crucibles and ink-stands of Giessen, and LIEBIG and his pupils, like the wandering knights of old, were shivering their lances against every one they met" (*loc. cit.*, p. v).

LIEBIG's criticisms of MULDER, which in many cases were mere quibblings, were directed chiefly against the Dutch chemist's views upon the proteins and humus. MULDER had coined the word "protein" to indicate a wide class of nitrogenous plant and animal constituents, whose great importance in nutrition he was among the earliest to recognize. To this class of compounds he assigned a basic constituent group of the general formula $C_{40}H_{31}N_5O_{12}$ (old equivalents), the differences in character of the individual proteins (albumen, fibrin, casein, etc.) being attributed to differences in what MULDER called the "primary arranging forces" (p. 73). Various multiples of the basic group, combined with one or more molecules of loosely attached sulfur and phosphorus, made up, according to MULDER, the composition of the various compound proteins. Thus casein was represented as $10(C_{40}H_{31}N_5O_{12}) + S$; Glutin, as $10(C_{40}H_{31}N_5O_{12}) + S_2$;

Fibrin and egg albumen as $10(\text{C}_{40}\text{H}_{31}\text{N}_5\text{O}_{12}) + \text{SP}$; and Blood Albumen as $10(\text{C}_{40}\text{H}_{31}\text{N}_5\text{O}_{12}) + \text{S}_2\text{P}$. By hydrolyzing albumen and other proteins with potash MULDER obtained several decomposition products which he classified as follows (p. 310), with their atomic composition (old equivalents) :—

	C	H	N	O
2 equivalents of leucin	24	24	2	8
2 equivalents of protid	26	18	2	8
2 equivalents of erythroprotid	26	16	2	10
4 equivalents of ammonia	0	12	4	0
2 equivalents of carbonic acid	2	0	0	4
1 equivalent of formic acid	2	1	0	3
	80	71	10	33
2 equivalents of protein ($\text{C}_{40}\text{H}_{31}\text{N}_5\text{O}_{12}$) +				
9 equivalents of water (HO) =	80	71	10	33

In commenting upon this table LIEBIG (1847) remarked as follows :—

"A glance at this equation is sufficient to show, that the agreement is as complete as possible. On one side we have the elements of proteine and of water, on the other, six products of decomposition; the sum of the elements being exactly equal on both sides; and yet a repetition of the experiment on which the equation is founded, teaches us that the whole explanation is utterly fallacious. For the chief product of this decomposition is a compound (possibly more than one compound) not precipitable by salts of lead; there is produced no formic acid, but oxalic acid, as well as valerianic and butyric acids; and in the case of fibrine, caseine, and the albumen of the serum of blood, there is formed a crystallisable body, tyrosine (I give this name to the substance described by me in the 'Annalen der Chemie und Pharmacie,' vol. LVII, p. 127), in all, therefore, five members, which are wanting in the equation. Moreover, according to the above equation, 100 parts of white of egg should yield 30 parts of leucine, whereas, in reality, we can obtain hardly 2 per cent. of that compound."

"Without possessing the gift of prophecy, we may safely predict that we shall have, in a few years, in place of the formulae which he has given for animal compounds, and which he regards as for ever established, entirely different formulae. It will fare with these analyses as with those which he has made of vegetable mucilage, of pectine, of glycocoll (sugar of gelatine), and other substances, for the accuracy of which the dexterity of the chemist is for a time regarded as a guarantee, but which cease to be considered accurate, when the substances analysed become the subject of more exact investigation.

"When such fallacious principles and methods of investigation are accompanied by erroneous theoretical views, which, while they refuse admission to the most convincing evidence of the truth, are defended with a violence and obstinacy proportioned to the feebleness of these views, the field of research becomes a stage on which the most selfish passions are brought into action; but, under such circumstances, progress is out of the question.

"A theoretical view in natural science is never absolutely true, it is only true for the period during which it prevails; it is the nearest and most exact expression of the knowledge and the observations of that period. In proportion as our knowledge is extended and changed, this expression of it is also extended and changed, and it ceases to be true for a later period, inasmuch as a number of newly acquired facts can no longer be included in it. But the case is very different with the so-called proteine theory, which cannot be regarded as one of the theoretical views just mentioned, since, being supported by observations both erroneous in themselves and misinterpreted as to their significance, it had no foundation in itself, and was never regarded, by those intimately acquainted with its chemical groundwork, as an expression of the knowledge of a given period."

The quotation from LIEBIG is a good illustration of the soundness of his philosophical and scientific views upon the one hand and of his vindictive unfair methods of criticism upon the other. Highly speculative formulas had been used by LIEBIG to an even greater extent than was attempted by MULDER, as for example in the conjectural reaction shown on pages 275-6 of the present book. In this case, as in many others, LIEBIG's criticisms can be quoted almost word for word against himself.

Other censorious comments by LIEBIG caused MULDER to publish in 1846 a very scathing "Reply to LIEBIG on the Chemistry of Animal and Vegetable Physiology" of which an English translation by FROMBERG was immediately printed in London. The controversy was an unfortunate one. MULDER's animosity became an obsession and all his future writings were tinged with a spirit of bitter hostility towards LIEBIG.

Another subject to which MULDER devoted much attention was the chemical composition of the cellular constituents of plants which he investigated both microscopically and chemically. The "Proof of a General Physiological Chemistry" is illustrated with many beautiful colored plates by MULDER's colleague, Professor HARTING, who employed differential staining to bring out the anatomical characteristics of various plant tissues. MULDER estimated the chemical constitution of the intermediate ligneous matter of vegetable cells by removing the protein, fat and other extractives with solvents and then subtracting from the elementary composition of the resultant fiber, the composition of its cellulose. He thus obtained (p. 424) for the spiral threads of *Agave americana* (using old equivalents):—

	C	H	O
Formula purified fibre	64	49	47
Formula cellulose	24	21	21
Formula woody matter by difference.....	40	28	26

The woody matter as thus calculated comprises not only the lignin but the pentosans and other hemicelluloses of the fiber whose existence was unknown in MULDER's time.

This hypothetical woody matter of MULDER's analysis was assumed by him to be the parent substance of the ulmin and other substances that constituted the humus of soils. The conversion into ulmin was supposed to take place in the decay of plant materials by the elimination of water as follows:—

	C	H	O
Woody matter	40	28	26
14 equivalents of water (HO).....		14	14
Ulmin	40	14	12

The ulmin thus formed is further decomposed according to MULDER

"into ulmic acid, humin, humic acid, geic acid, apocrenic acid and at last into crenic acid. Of these seven substances, the five acids can all be combined with bases, and thus rendered soluble in water. These are the organic substances—and as yet we know of no others—that are absorbed by plants as food. They are present in every soil, and

apparently they all enter through the tender roots into the plants, where they are to perform important functions.

"The greater part, and perhaps the whole, of the ammonia which plants absorb from the soil is supplied to them by means of these organic acids. Experience has taught us, that salts of ammonia are injurious to plants, unless they are combined with these organic acids, and that when thus combined—as they are in liquid and other manures, in decayed sheeps', cows', or pigeons' dung—they are of great benefit to plants. Whatever salt of ammonia is added to the soil, it can be separated from it from the moment that the admixture has taken place in no other form except in that of ulmate, humate, geate, apocrenate, or crenate of ammonia, provided the soil contains a sufficient quantity of decayed organic matter. Upon this principle, it has been, from the earliest times, the practice of the art of agriculture to bring manure into a state of putrefaction, by which the mixture of the five different ammoniacal salts, just mentioned, is prepared, and food is directly supplied to plants. The urine of men and animals, and guano—that is to say, the urea, uric acid, or hippuric acid which these substances contain, or whatever other substances producing ammonia may be employed—all combine in the form of ammonia with the above-named five acids in the soil, before they serve as food for plants" (pp. 659–60).

The above quotation is the essence of MULDER's famous humus theory of soil fertility which was combated so strenuously by LIEBIG and which in the writings of MULDER's pupils found a wide acceptance. It formed the basis of the chemical views expressed by SAMUEL L. DANA in his famous "Muck Manual" (5th ed., New York, 1855) for several decades the *vademecum* of farmers in New England and New York.

MULDER, however, was not the originator, but the chief defender of the old theory that the organic matter of soils was a principal source of plant food. The beneficial effects of organic manures upon crop growth had been recognized by Greek and Roman agricultural writers but scientific explanations of these effects did not begin to appear until the eighteenth century. STAHL, following BECHER, attributed the fertility of soils to a phlogistic fatness (pinguedo). J. A. KÜLBEL in his "Cause de la fertilité des terres" (Bordeaux, 1741) assumed that a fatty magma (magma unguinosum), occurring in humus, was essential to plant growth and the main cause of soil fertility. FRANCIS HOME in his "Principles of Agriculture and Vegetation" (Edinburgh, 1757) adopted a somewhat similar view, holding that oil "is communicated to the ground by all the vegetable and animal manures." This idea of an oily or fatty principle of fertility was emphasized also by WALLERIUS in his "Agriculturae fundamenta chemica" (Upsala, 1761). DAVY stressed the importance of humus and the need of bringing it into solution by oxidation and fermentation before it could be used by plants. THAER and DE CANDOLLE were other authorities who, by their eminence, gave much additional support to the belief that the fertility of a soil depended largely upon its supply of humus.

The chemical study of the organic matter of soils was slow in developing and, as so frequently happens in science, an incentive came from other fields of research. In 1797 the French chemist VAUQUELIN called attention to the properties of a peculiar gum-like exudation from the bark of an elm tree for which in 1813 the British chemist THOMSON proposed the name ulmin (from the Latin word *ulmus* meaning elm). The similarity in properties between ulmin and the dark-colored organic matter extracted from soils by means of alkali caused the name ulmin to be given to the latter

substance also. Its property of forming compounds with bases caused the term ulmic acid to be introduced. The synonymous term humic acid for the alkali-soluble organic matter of soils was proposed by SPRENGEL in 1826 and so confusion arose as to the exact meaning of the terms employed by different writers. SPRENGEL investigated the various salts of his humic acid and endeavored to determine their chemical composition. His methods were widely employed and continued in use for many decades to come.

Meanwhile substances similar to the organic matter of soils had been prepared artificially by decomposing starch and sugar with hydrochloric and sulfuric acids first in 1819 by BRACONNOT who termed his product "artificial ulmin" and then later in 1830 by BOULLAY who introduced the term "artificial ulmic acid." These observations suggested that the transformations of vegetable matter in the soil to humus or ulmin were analogous to the decompositions of carbohydrates produced artificially in the laboratory.

BERZELIUS, recognizing that the word "ulmin" was being loosely applied to substances of different character and origin, suggested in 1832 that the terms "gein" (from the Greek word $\gamma\eta$ meaning earth) and "geic" acid be employed to designate the organic alkali-soluble constituents of the soil. Although BERZELIUS afterwards abandoned the use of these terms, the names "gein" and "geic acid" were perpetuated by DANA in the various editions of his "Muck Manual."

In 1833 BERZELIUS isolated from the water of the Porla spring the copper salts of two organic acids which from their source he named "crenic" and "apocrenic" acids (from the Greek word $\kappa\rho\eta\nu\eta$ meaning spring). These complexes he believed to be constituents also of the organic matter of soils.

MULDER, who was a pupil of BERZELIUS, continued the latter's work upon the humus matter of soils and accepting the existence of its seven hypothetical components, ulmin, humin, and ulmic, humic, geic, apocrenic and crenic acids, attempted to establish the importance and necessity of these for plant nutrition. LIEBIG and other opponents of the humic theory held that the only benefit resulting from the presence of organic matter in the soil was the constant supply of carbon dioxide which it yielded, during decay, to the growing plant. MULDER did not deny this benefit but insisted also that the humus matter of the soil in the form of the soluble ammonium salts of ulmic, humic, geic, apocrenic and crenic acids was directly absorbed by the rootlets of plants to produce protein, the elaboration of which he attempted to illustrate (p. 668) by the following diagram (old equivalents) : —

		C	H	N	O
1 equivalent of humic acid	=	40	12	—	12
5 equivalents of ammonia	=	—	15	5	—
4 equivalents of water	=	—	4	—	4
		40	31	5	16
1 equivalent of protein+					
4 equivalents of O	=	40	31	5	12 + 40

The supposed generation and fixation of ammonia from contact of atmospheric nitrogen with the humus of the soil was an essential part of

MULDER's theory of soil fertility. He assumed that the nitrogen of the air in contact with decaying humus combined with the hydrogen of the latter to form ammonia. Ulmic acid $C_{40}H_{14}O_{12}$ by the loss of hydrogen was thus changed to humic acid $C_{40}H_{12}O_{12}$; the latter by oxidation was converted into geic acid $C_{40}H_{12}O_{14}$ and this again by further oxidation and condensation gave rise to the penta-basic apocrenic acid $C_{48}H_{12}O_{24}$ which by further oxidation and cleavage yielded the final member of the series, crenic acid $C_{24}H_{12}O_{16}$. The latter on further oxidation was supposed to break down into carbon dioxide and water the ultimate products of humus decomposition (pp. 146-72). According to MULDER the ammonia which was formed by the union of atmospheric nitrogen with the hydrogen of humus not only formed the soluble salts of ulmic, humic, geic, apocrenic, and crenic acids but a part of it was oxidized in the soil to nitric acid. This scheme of nitrification was MULDER's explanation of the formation in nature of nitrates where no putrefying nitrogenous substances were present (p. 58).

An additional argument employed by MULDER and other advocates of the humus theory of plant nutrition is the assimilation of organic matter from decaying wood, etc., by various saprophytic fungi. If the lower plants can function in this way, reasoned MULDER, there is no reason to deny the same faculty to higher vegetation.

The cycle of operations which take place in the vegetable kingdom was thus pictured by MULDER: —

"The carbonic acid of the air is condensed and decomposed by the leaves; this carbonic acid along with water is employed by the leaves to form non-nitrogenous bodies; the leaves are shed; they putrefy and form humic and crenic acids; ammonia is produced in the soil from water and the constituents of the air; the ammonia combines with these acids and forms humates and crenates of ammonia; these salts enter into the plant through the root; from these salts nitrogenous substances are formed in the root; these substances are carried up into the leaves and fruits; part of them descends again, along with the products of the decomposition of carbonic acid, to form wood. The leaves are shed and decay, and with this the cycle recommences" (p. 690).

The rejected humus theory, which had its advocates even down to the commencement of the present century, played a most important rôle in the history of agricultural chemistry. Not one of the components of humus, reported by the old writers and enumerated by MULDER, has ever been isolated as a pure compound and as for assigning chemical formulas to the constituents of humus agricultural chemists are today as much in the dark as they were a century ago.

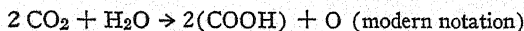
The fact that plants could be grown to perfect maturity in earth, or water cultures, that were completely devoid of organic matter, caused LIEBIG and other opponents of the humus theory to deny any benefit to crops from this constituent of soil, except in so far as it served as a source of carbon dioxide to the growing plant. This view has since been proved to be as untenable as the opposite belief in the value of humus as a plant food. In addition to its rôle in improving tilth, moisture-retaining capacity and other physical characteristics of soils it is now recognized that the decaying organic matter of the soil is a medium for the development of numerous groups of beneficial micro-organisms which by their activity assist not only in the formation of carbon dioxide, ammonia, and nitrates

but also in unlocking phosphorus, potassium, calcium and other nutritive elements from their insoluble combinations in forms that are available to the growth of plants. The demonstration of these facts was impossible, however, in the time of MULDER and LIEBIG and had to await the development of the later science of soil microbiology.

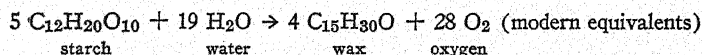
Another theory frequently proclaimed by MULDER relates to the phytochemical processes by which plants give off oxygen. He held this to be a characteristic reaction of all plant organs and not a sole peculiarity of the green chlorophyll-bearing tissues, which are concerned with the assimilation of carbon dioxide.

"It is an undoubted fact," writes MULDER, "that the parts that become green, absorb carbonic acid, and emit chiefly oxygen in its place. This is actually a two-fold function; for there is no connexion between the absorption of carbonic acid, and the emission of oxygen. The first is an independent function, regulated by the same laws as those which regulate the absorption of gases by liquids; whilst the emission of oxygen is the result of a general chemical conversion of the vegetable substances, to combinations in a lower state of oxidation,—a conversion which the carbonic acid absorbed likewise undergoes" (p. 678).

Numerous illustrations of the reactions by which oxygen is evolved by plant organs are cited by MULDER. Thus the production of oxalic acid, which he wrongly assumes to be formed by the condensation of two molecules of carbon dioxide with one molecule of water is supposed to take place as follows (p. 803):—



In the same way the wax in the leaves of all plants was produced according to MULDER from starch with the liberation of oxygen (p. 289).



The formation of protein from humic acid, ammonia and water (p. 668) and of quinine from ulmic acid, ammonia, carbon dioxide and water (p. 800) are cited by MULDER among other examples of the same type of reaction.

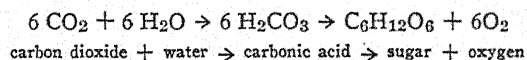
This contradiction of the fundamental law of SENEBIER that the presence of carbon dioxide is an indispensable condition for the evolution of oxygen from the green tissues of plants was based, however, upon purely speculative grounds and did not receive general acceptance. An apparent confirmation of MULDER's statement that "there is no connexion between the absorption of carbonic acid and the emission of oxygen" was previously noted in discussing the observations of DE SAUSSURE and of ADOLF MAYER that fleshy-leaved plants can liberate oxygen in air deprived of carbon dioxide (p. 198 of this book). The explanation of the evolution of oxygen in such cases as the result of a decomposition in sunlight of plant acids, that serve as a concealed internal source of carbon dioxide which is then utilized photosynthetically in the usual way, can be viewed as a partial confirmation of MULDER's theory that "oxygen is a product of the change of materials among substances existing in the plant" (p. 779). This oxygen, according to MULDER,

"is dissolved in the sap of plants in the same way as was explained with regard to the nitrogen; and it remains in this sap until it can be exchanged with another gas through a cellular membrane, according to the laws of diffusion. Thus it may accumulate in

the air-cavities, from which it is expelled through the stomata and discharged into the atmosphere.

"It has been erroneously stated that the carbonic acid, after having entered into the green parts, leaves its carbon behind and gives off its oxygen. Not a single proof can now be adduced to show that such a direct action takes place. We have, on the contrary, every reason at present to reject this idea as unchemical. The carbonic acid may combine with the elements of water, and form one or more substances, which are as yet unknown or it may unite with existing bodies to form new products;—in a word, the carbonic acid from the atmosphere, which is introduced through the stomata into the air canals, and through them into the plant, close to the cells which are filled with sap,—the carbonic acid, replacing the oxygen and nitrogen in the sap, is not, as has been assumed, suddenly decomposed into oxygen, which returns, and carbon, which enters into immediate combination" (p. 780).

MULDER's view that the carbon dioxide of the air in the photosynthetic process is not suddenly decomposed into oxygen is substantially correct. A part of the oxygen evolved by a leaf may have come from the photosynthetic decomposition of organic acids formed in the interior organs of the plant and thus have no connection with the carbon dioxide that is being simultaneously assimilated. The fact, however, that the ratio of oxygen evolved to the carbon dioxide absorbed by the leaves of plants in sunlight is found experimentally to be almost unity lends support to the view that by far the greater part of the photosynthetic reaction proceeds in a manner analogous to the fundamental equation



It will be noted that the problems relating to the proteins, the hemicelluloses, soil humus, and the oxidation-reduction processes of living cells, which MULDER selected for consideration are still far from being completely solved. They are among the most difficult problems of agricultural chemistry and MULDER deserves credit for having focused the attention of investigators upon the fundamental problems of greatest significance in agricultural chemistry. He should not be criticized too severely for his undue use of speculative equations, the conclusions of which he regarded as only indicative and not as final. As he modestly states in a significant paragraph: —

"Science, therefore, will not advance one step by such indications of the existence of mere mutual relations between the various vegetable substances; and as we are yet unacquainted with the specific mode of their production, it will be best to confess our ignorance on this point, and to rest satisfied with the little that we at present know—patiently waiting for what will be discovered in future" (p. 801).

MULDER was a voluminous writer and published a large number of works relating to chemical analyses, miscellaneous laboratory investigations and the chemistry of salt, wine and beer. In 1860 he published his important "Scheikunde der bouwbare Aarde" (Chemistry of tillable Soil) a compendious work in four volumes. Its subject matter falls outside the period discussed in this volume. Two German translations of the book (Chemie der Ackerkrume) were published in 1861-63, one by C. GRIMM at Leipzig in two volumes and the other by J. MÜLLER at Berlin in three volumes. A sympathetic review of this work in the light of later knowledge

was published by J. M. VAN BEMMELEN (1901). In 1864 MULDER published at Rotterdam his "Contributions to the History of Chemically Combined Water" of which a French translation was printed at Haarlem. A German translation of MULDER's "Chemistry of the Drying Oils, their Preparation and Technical Use in the Arts and Manufactures" (*Chemie der austrocknenden Oele, ihre Bereitung und ihre technische Anwendung in Künsten und Gewerben*) by J. MÜLLER was published at Berlin in 1867.

After retirement from his professorship in 1868 MULDER made no further contributions to the science of agricultural chemistry and his name lapsed soon into forgetfulness. He had the misfortune to leave no school of young chemists, as did LIEBIG and BOUSSINGAULT, to perpetuate his influence and teachings. It was a tragic effect of his long controversies with LIEBIG that much of his energy was diverted from more productive efforts. Later opinion which came to recognize the unfairness of many of LIEBIG's criticisms has taken a more appreciative view of MULDER's work. A few extracts from a comparative estimate of the work of MULDER and LIEBIG by VAN BEMMELEN (1901b) are quoted in conclusion:—

"LIEBIG expounded his system in assertive dogmas which because of their tone of conviction transformed agricultural science and gave it farther direction. In elucidating phenomena he gave chemical explanations which on appearance seemed to be perfectly satisfactory and which thus shut off further inquiry or at least chained it fast to LIEBIG's doctrines.

"MULDER endeavored on the other hand to illuminate every side of each problem and not to confine it with any bonds of dogmatism. Every moment he makes evident the need of science. He tries indeed to explain many problems—yes too many—as is especially evident in his doctrine of the gelatinous silicates—yet always in a way that does not imprison but liberates the points at issue. On almost every page of his book his explanations and expositions give stimulus to further research. If LIEBIG constantly rejects the old farm-practices, MULDER turns them to good account.

"It was not MULDER, but LIEBIG, who controlled the direction of research in Germany and elsewhere and only slowly has research been liberated from this influence. We must, however, concede the great value of LIEBIG's efforts in giving such a powerful impulse to agricultural chemistry and by means of his oracular sentences in awaking interest and life—a life that has given existence to the numerous experiment stations that now cover Germany and other Germanic countries and are imitated also in England, Belgium and France. . . .

"However, it seems to me that it would have been much more fortunate for agricultural chemistry if MULDER's ideas and not LIEBIG's had gained followers. The mistakes of LIEBIG must all be refuted and are still being refuted. They gave at first an unfortunate trend to research, although research, as goes without saying, has always brought more light and helped find the good way back. . . .

"Although MULDER's book was translated into German, his doctrines have exerted but little influence. Yet they were the better ones, as is evident from what has been said and as the latest handbooks on agricultural chemistry can show. It can be affirmed that recent progress in agricultural chemistry and physics, although not yet relatively great, has taken place along MULDER's, and not along LIEBIG's, lines. Upon the continued investigation of the gelatinous parts of the soil (humus and silicates) and the chemical processes that occur therein, on the one hand, and upon greater attention to the findings and rules of practical agriculture, on the other, a great part of the future progress in agricultural science will depend."

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Justus von Liebig (1803-73): — In the various books upon the chemistry of crops and soils by DE SAUSSURE, DAVY, CHAPTAL, SCHÜBLER, SPRENGEL and other writers, which appeared between the years 1800 and 1840, a large number of the fundamental principles of agricultural chemistry had been elucidated but as yet no one had attempted to sift the collections of heterogeneous data and compile therefrom a definite system of agricultural chemistry. The codifying of a science in the period of its early development is likely to have a double influence; it may be highly beneficial, on the one hand, in helping to divest the science of false ideas and unessential trappings; it may be highly detrimental, on the other hand, in giving research a wrong direction by setting up faulty hypotheses as fixed principles of guidance. This double influence is nowhere better shown than in LIEBIG's "Organische Chemie in ihrer Anwendung auf Agricultur und Physiologie," a work that attained a greater prominence in agriculture than any other chemical treatise.

LIEBIG was born at Darmstadt, Germany, the son of a dealer in dye-stuffs, in the making of which the young boy obtained his first introduction to practical chemistry. He acquired also at an early age much miscellaneous chemical information from the various books to which he had access. In 1819 LIEBIG entered the University of Bonn and studied chemistry under KASTNER whom he afterwards followed to Erlangen where he obtained his Ph.D. degree in 1822. The young graduate then proceeded to Paris where he completed his chemical studies under GAY-LUSSAC and THENARD. On returning to Germany LIEBIG, on the recommendation of ALEXANDER VON HUMBOLDT, was appointed in 1824 Professor of Chemistry at the University of Giessen where he soon established the first research laboratory for students of organic chemistry. His fame as teacher and investigator soon attracted pupils from all parts of the world to Giessen where they imbibed not only the methods but the zealous spirit and energy of their leader.

One of the first important results of LIEBIG's work was the development of new apparatus for determining accurately the elementary composition of organic substances. His investigations in this field added greatly to the knowledge of the constitution of many compounds that occur in agricultural

products such as malic acid, asparagin, aspartic acid, uric acid, hippuric acid and the plant alkaloids. Of particular importance was the joint research which WÖHLER and LIEBIG (1832) published on oil of bitter almonds (benzaldehyde). They found that the constituent group (the benzoyl radicle C_7H_5O) of this oil passed unchanged into benzoic acid and all its derivatives, and they thus laid the foundation of the theory of compound radicles—a discovery that was hailed by BERZELIUS (1832) “as the beginning of a new day in plant chemistry.” Of equal importance was the investigation that WÖHLER and LIEBIG (1837) then undertook on the crystalline substance amygdalin which occurs in bitter almonds. It was found that a ferment, or as would now be said an enzyme, from almonds, which they called emulsin, decomposed amygdalin into oil of bitter almonds, prussic acid and glucose. The constitution of an important member of the group of plant substances called glucosides was thus made known.

A research of great importance in its agricultural chemical aspects was the study of LIEBIG (1837) on vinegar making. The process by which the alcohol of wine, cider and beer was converted into acetic acid remained in obscurity until LIEBIG showed that the first step in this change was the conversion of the alcohol into an intermediary oxidation product aldehyde which he for the first time isolated and identified.

Another factor of great importance in extending LIEBIG's influence was his participation in 1832 in founding the *Annalen der Pharmazie* which offered a convenient means for the publication of his numerous papers. This journal in 1840 was reorganized as the *Annalen der Chemie und Pharmazie* under the joint editorship of LIEBIG and WÖHLER. It quickly became the leading chemical publication of the world and in it were published many papers of great importance to the future development of plant and animal chemistry.

In the papers published in the *Annalen* between 1832 and 1840, the inception of LIEBIG's interest in agricultural chemistry can be traced. This is shown not only in LIEBIG's own articles on methods of analysis, on the alkaloids and organic acids of plants, and on other related subjects, but in the articles which he reproduced from other journals, such as the paper of MACAIRE-PRINSEP (1833) on crop rotation and root excretions, the article of SPRENGEL (1835) on the ash constituents of wood, and the contribution of BOUSSINGAULT (1837) on the valuation of cattle feeds. These articles helped LIEBIG in preparing the groundwork of his later book.

LIEBIG had now become the recognized leader in organic chemistry and his reputation in this field led to an invitation by the chemical section of the British Association for the Advancement of Science to present at its 1840 meeting a report upon the present state of Organic Chemistry. This report was the basis of LIEBIG's famous book “Organic Chemistry in its Applications to Agriculture and Physiology” of which two editions, the German at Brunswick and the English translation by LIEBIG's pupil LYON PLAYFAIR at London, were published in 1840. The immense popularity of the book is indicated by the fact that before 1848, it had gone through 17 different editions and translations, 4 in Germany, 4 in England, 2 in America, 2 in France and 1 each in Denmark, Holland, Italy, Poland and Russia. The work was constantly revised by LIEBIG; the ninth German edition was pub-

lished at Brunswick in 1876 three years after LIEBIG's death. The book owed much of its wide popularity to the influence of LIEBIG's many pupils in all parts of the world. It is to PLAYFAIR's 1840 English edition that the following page references (unless otherwise stated) pertain.

LIEBIG's high standing as an organic chemist did not qualify him, however, to be an authority on agricultural chemistry. While his work as analyst, teacher and editor gave him a wide intimate acquaintance with the chemistry of plant and animal substances, he lacked that practical experience with farm operations which was the strong endowment of his contemporary, BOUSSINGAULT. The first edition of LIEBIG's book on agricultural chemistry is, therefore, largely a critical review of preexisting knowledge with the selection and inculcation of those principles which appeared to LIEBIG as the most scientific and plausible. The book contains over two hundred references to the work of approximately a hundred different authors. Chief among these writers is THÉODORE DE SAUSSURE whom LIEBIG quotes no less than 24 times. BOUSSINGAULT, SPRENGEL, SCHÜBLER, BERZELIUS, DE CANDOLLE, GAY-LUSSAC, THENARD, and DAVY are also among the authorities whom he consulted. The absence of much experimental work of his own in the book caused BERZELIUS (1842) to make the provoking remark: —

"BOUSSINGAULT covers the same field as LIEBIG but BOUSSINGAULT takes the hard tiresome way of answering every question by one or more experiments. He gives his answers not so quickly but they are reliable."

LIEBIG's main purpose in writing the book is expressed in the dedication to the British Association.

"I have endeavored to develop, in a manner correspondent to the present state of science, the fundamental principles of chemistry in general, and the laws of organic chemistry in particular, in their applications to agriculture and physiology; to the causes of fermentation, decay, and putrefaction; to the vinous and acetous fermentations, and to nitrification. The conversion of woody fibre into wood- and mineral-coal, the nature of poisons, contagions and miasms, and the causes of their action on the living organism, have been elucidated in their chemical relations.

"I shall be happy if I succeed in attracting the attention of men of science to subjects which so well merit to engage their talents and energies. Perfect agriculture is the true foundation of all trade and industry—it is the foundation of the riches of states. But a rational system of agriculture cannot be formed without the application of scientific principles; for such a system must be based on an exact acquaintance with the means of nutrition of vegetables, and with the influence of soils and action of manure upon them. This knowledge we must seek from chemistry, which teaches the mode of investigating the composition and of studying the characters of the different substances from which plants derive their nourishment. . . ."

"Since the time of the immortal author of the 'Agricultural Chemistry' no chemist has occupied himself in studying the applications of chemical principles to the growth of vegetables, and to organic processes. I have endeavoured to follow the path marked out by Sir HUMPHRY DAVY, who based his conclusions only on that which was capable of inquiry and proof. This is the path of true philosophical inquiry, which promises to lead us to truth—the proper object of our research" (pp. vi-ix).

LIEBIG's assertion, that until his time no one since DAVY had "occupied himself in studying the applications of chemical principles to the growth of vegetables" is abundantly contradicted by the names of the authorities to whom he refers in his book and by articles in scientific journals including his own *Annalen*. It must be recognized that LIEBIG, here as in many other places, wrote as a propagandist and that absolute accuracy of statement on

his part is not always to be expected. His tendency to exaggerate, or to understate, must constantly be borne in mind.

LIEBIG, like SENEBIER in 1783, felt called upon to defend the employment of chemistry in the study of plant and animal life.

"In botany the talent and labour of inquirers has been wholly spent in the examination of form and structure; chemistry and physics have not been allowed to sit in council upon the explanation of the most simple processes; their experience and their laws have not been employed, though the most powerful means of help in the acquirement of true knowledge. They have not been used, because their study has been neglected.

"All discoveries in physics and in chemistry, all explanations of chemists, must remain without fruit and useless, because, even to the great leaders in physiology, carbonic acid, ammonia, acids, and bases, are sounds without meaning, words without sense, terms of an unknown language, which awaken no thoughts and no associations. They treat these sciences like the vulgar, who despise a foreign literature in exact proportion to their ignorance of it; since even when they have had some acquaintance with them, they have not understood their spirit and application" (p. 35).

LIEBIG's criticism of the botanists and physiologists is too severe. Carbonic acid, ammonia and other chemical terms were certainly not words without sense to such a writer as DE CANDOLLE who fully recognized the importance of chemistry in studying the phenomena of plant life and to whom LIEBIG was especially indebted for some of his ideas. Similar slighting remarks were made by LIEBIG against mathematicians and as a result of such attacks much needless hostility was provoked against him and his new school of chemistry.

LIEBIG's "Organic Chemistry in its Applications to Agriculture and Physiology" is divided into two parts, the first of which deals with the chemical processes in the nutrition of vegetables and the second with the chemical processes of fermentation, decay and putrefaction. The following brief summary of the contents of the book is presented:

LIEBIG mentions as the three basic chemical requirements of crops: (1) substances containing carbon and nitrogen and capable of yielding these elements to the growing crop; (2) water and its elements; (3) a soil that can furnish the inorganic matters essential to plant life (p. 4).

The theory held by many chemists that soil fertility depended upon a sufficient supply of humus was strongly combated by LIEBIG. Plants, as had been proved by the early work of SENEBIER, have the faculty of assimilating carbon from the carbonic acid of the air, and humus, according to LIEBIG, is useful only in so far as its continued decay provides a supply of carbon dioxide for the growing plant (p. 47).

"Humus does not nourish plants, by being taken up and assimilated in its unaltered state but by presenting a slow and lasting source of carbonic acid, which is absorbed by the roots and is the principal nutriment of young plants at a time when, being destitute of leaves, they are unable to extract food from the atmosphere" (pp. 59-60).

LIEBIG's theory that plants assimilate carbonic acid through the roots as well as through the leaves, although disputed by some plant physiologists, has recently been revived. The nutritive materials of the young plantlet are the organic and inorganic substances of the seed and this fact was used by the defenders of the humus theory as an argument that fully grown plants could derive organic sustenance from the soil. LIEBIG announced that

"All the hydrogen necessary for the formation of an organic compound is supplied to a plant by the decomposition of water. The process of assimilation, in its most simple form, consists in the extraction of hydrogen from water and carbon from carbonic acid, in consequence of which, either all the oxygen of the water and carbonic acid is separated, as in the formation of caoutchouc, the volatile oils which contain no oxygen, and other similar substances, or only a part of it is exhaled.

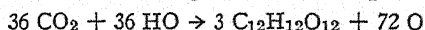
"The known composition of the organic compounds most generally present in vegetables, enables us to state in definite proportions the quantity of oxygen separated during their formation."

Production of organic substances from carbon dioxide and water (LIEBIG)

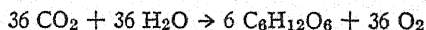
EQUIVALENTS OF CARBONIC ACID	EQUIVALENTS OF REACTING WATER	SUBSTANCE PRODUCED	EQUIVALENTS OF OXYGEN LIBERATED
36	22	Woody fire	72
36	36	Sugar	72
36	30	Starch	72
36	16	Tannic acid	64
36	18	Tartaric acid	45
36	18	Malic acid	54
36	24	Oil of turpentine	84

(pp. 65-6)

Great confusion in the expression of chemical reactions prevailed until after the Carlsruhe conference of 1860, equivalents, molecules and atoms being used indiscriminately. The reaction for formation of sugar from carbon dioxide and water according to LIEBIG's representation is



When the modern theory of valence was introduced and a due allowance made to the neglected hypothesis of AVOGADRO, the atomic weights of oxygen, carbon, sulfur and other atoms were doubled. The above photosynthetic equation of LIEBIG then became



which indicates that for each volume or molecule of carbon dioxide assimilated an equal amount of oxygen is evolved.

The elementary cycle of carbon and hydrogen was thus summarized by LIEBIG: —

"During the progress of growth, plants appropriate carbon in the form of carbonic acid, and hydrogen from the decomposition of water, the oxygen of which is set free, together with a part or all of that contained in the carbonic acid. In the process of putrefaction, a quantity of water, exactly corresponding to that of the hydrogen, is again formed by extraction of oxygen from the air; while all the oxygen of the organic matter is returned to the atmosphere in the form of carbonic acid" (pp. 68-9).

LIEBIG discusses next the important question of the origin and assimilation by crops of nitrogen, the element which is needed for the formation of albumen, gluten, and other nitrogenous compounds so essential for animal food.

"Let us picture to ourselves the condition of a well-cultured farm, so large as to be independent of assistance from other quarters. On this extent of land there is a certain quantity of nitrogen contained both in the corn and fruit which it produces, and in the

men and animals which feed upon them, and also in their excrements. We shall suppose this quantity to be known. The land is cultivated without the importation of any foreign substance containing nitrogen. Now, the products of this farm must be exchanged every year for money, and other necessities of life, for bodies therefore which contain no nitrogen. A certain proportion of nitrogen is exported with corn and cattle; and this exportation takes place every year, without the smallest compensation; yet after a given number of years, the quantity of nitrogen will be found to have increased. Whence, we may ask, comes this increase of nitrogen? The nitrogen in the excrements cannot reproduce itself, and the earth cannot yield it. Plants, and consequently animals, must, therefore, derive their nitrogen from the atmosphere" (pp. 71-2).

The nitrogen thus acquired was thought by LIEBIG to have been derived entirely from atmospheric ammonia produced by the decay of nitrogenous animal and vegetable matter.

"The nitrogen of putrified animals is contained in the atmosphere as ammonia, in the form of a gas which is capable of entering into combination with carbonic acid, and of forming a volatile salt. Ammonia in its gaseous form as well as all its volatile compounds are of extreme solubility in water. Ammonia, therefore, cannot remain long in the atmosphere, as every shower of rain must condense it, and convey it to the surface of the earth. Hence, also, rain-water must, at all times, contain ammonia, though not always in equal quantity" (p. 73).

"Wild plants obtain more nitrogen from the atmosphere in the form of ammonia than they require for their growth, for the water which evaporates through their leaves and blossoms, emits, after some time, a putrid smell, a peculiarity possessed only by such bodies as contain nitrogen. Cultivated plants receive the same quantity of nitrogen from the atmosphere as trees, shrubs, and other wild plants; but this is not sufficient for the purposes of agriculture" (p. 85).

In subsequent editions of his book LIEBIG very unwisely reversed this last statement so as to read "and this is quite sufficient for the purposes of agriculture"—an unfortunate change which, with other unqualified assertions, was severely criticized by the English investigators J. B. LAWES and J. H. GILBERT (1855).

It is in the part of his book upon the inorganic constituents of plants that LIEBIG develops the so-called "Mineral Theory of Manures" for which he became so widely known.

"Carbonic acid, water and ammonia, are necessary for the existence of plants, because they contain the elements from which their organs are formed; but other substances are likewise requisite for the formation of certain organs destined for special functions peculiar to each family of plants. Plants obtain these substances from inorganic nature. In the ashes left after the incineration of plants, the same substances are found*, although in a changed condition.

"Many of these inorganic constituents vary according to the soil in which the plants grow, but a certain number of them are indispensable to their development. All substances in solution in a soil are absorbed by the roots of plants, exactly as a sponge imbibes a liquid, and all that it contains, without selection. The substances thus conveyed to plants are retained in greater or less quantity, or are entirely separated when not suited for assimilation" (pp. 92-3).

The chief function of the alkalis and alkaline earths in plant nutrition, according to LIEBIG, is to neutralize the various acids that occur in the cellular juices. In this connection he remarked:—

* Incorrectly translated "formed" in PLAYFAIR's edition.

"In order to understand this subject clearly, it will be necessary to bear in mind, that any one of the alkaline bases may be submitted for another, the action of all being the same. Our conclusion is, therefore, by no means endangered by the existence of a particular alkali in one plant, which may be absent in others of the same species. If this inference be correct, the absent alkali or earth must be supplied by one similar in its mode of action, or in other words, by an equivalent of another base. The number of equivalents of these various bases, which may be combined with a certain portion of acid, must necessarily be the same, and, therefore, the amount of oxygen contained in them must remain unchanged, under all circumstances, and on whatever soil they grow.

"Of course, this argument refers only to those alkaline bases, which in the form of organic salts form constituents of the plants. Now, these salts are preserved in the ashes of plants, as carbonates, the quantity of which can be easily ascertained" (p. 95).

LIEBIG was rightly criticized by SPRENGEL for supposing that one absent alkali or earth in a plant could be supplied by an equivalent of another base. The essential basic elements potassium, calcium and magnesium have other physiological functions than that of neutralizing free organic acids. The hypothesis of constant oxygen equivalent in the carbonates of plant ashes is untenable.

The old view, sponsored by THAER and earlier writers, that mineral matter could be produced within the plant by vital forces, was rejected by LIEBIG (pp. 144-5), as it had been previously by DE SAUSSURE, SPRENGEL, WIEGMANN and others.

Phosphoric acid and the bases potash, soda, lime and magnesia are found in the ashes of all crops and these according to LIEBIG must be restored to the land for the maintenance of fertility in exhausted soils.

"Air, water, and the change of temperature prepare the different species of rocks for yielding to plants the alkalies which they contain. A soil which has been exposed for centuries to all the influences which effect the disintegration of rocks, but from which the alkalies have not been removed, will be able to afford the means of nourishment to those vegetables which require alkalies for its growth during many years; but it must gradually become exhausted, unless those alkalies which have been removed are again replaced; a period, therefore, will arrive, when it will be necessary to expose it, from time to time, to a further disintegration, in order to obtain a new supply of soluble alkalies. For small as is the quantity of alkali which plants require, it is nevertheless quite indispensable for their perfect development. But when one or more years have elapsed without any alkalies having been extracted from the soil, a new harvest may be expected.

"The first colonists of Virginia found a country, the soil of which was similar to that mentioned above; harvests of wheat and tobacco were obtained for a century from one and the same field without the aid of manure, but now whole districts are converted into unfruitful pasture land, which without manure produces neither wheat nor tobacco. From every acre of this land, there were removed in the space of one hundred years 1200 lbs. of alkalies in leaves, grain, and straw; it became unfruitful therefore, because it was deprived of every particle of alkali, which had been reduced to a soluble state, and because that which was rendered soluble again in the space of one year, was not sufficient to satisfy the demands of the plants. Almost all the cultivated land in Europe is in this condition; fallow is the term applied to land left at rest for further disintegration. It is the greatest possible mistake to suppose that the temporary diminution of fertility in a soil is owing to the loss of humus; it is the mere consequence of the exhaustion of the alkalies" (pp. 148-9).

The amount of ash obtained by incineration was incorrectly used by LIEBIG as a comparative measure of the fertilizer requirements of different crops.

"One hundred parts of the stalks of wheat yield 15.5 parts of ashes (H. DAVY); the same quantity of the dry stalks of barley, 8.54 parts (SCHERADER); and one hundred parts of the stalks of oats, only 4.42;—the ashes of all these are of the same composition.

"We have in these facts a clear proof of what plants require for their growth. Upon the same field, which will yield only one harvest of wheat, two crops of barley and three of oats may be raised" (pp. 152-3).

These conclusions of LIEBIG were not only faulty in principle but they were further vitiated, as in many other parts of his book, by the acceptance of unreliable analytical data. When LIEBIG wrote the above passage he had not begun to make the analyses of plant ashes that were pursued so energetically in his laboratory two years later. Criticisms of his book obliged him to submit his unconfirmed statements to a rigid analytical verification and when this was done many erroneous passages, including the one just quoted, were eliminated from future editions of his work. In a letter dated Giessen, May 16, 1843, LIEBIG wrote:—

"We are occupied here with nothing but ash-analyses. But much is yet required in order to obtain perfectly reliable results. Ashes of crops grown on the most different kinds of soils must be investigated in order to determine definitely their constant constituents" (VOGEL, 1874a).

LIEBIG should have realized earlier the importance of verifying his statements. Because of his failure to do so the first edition of his book on agricultural chemistry is a much less finished and accurate work than the first edition of BOUSSINGAULT'S "Economie Rurale." The dogmatic tone of infallibility with which he promulgated his doctrines is also in marked contrast to the cautious unassertive style of the French investigator.

The fertilizing action of the excreta, bones, etc. of animals were attributed by LIEBIG to their inorganic constituents:—

"The peculiar action, then, of the solid excrements is limited to their inorganic constituents, which thus restore to a soil that which is removed in the form of corn, roots, or grain. When we manure land with the dung of the cow or sheep, we supply it with silicate of potash and some salts of phosphoric acid. In human faeces we give it the phosphates of lime and magnesia; and in those of the horse, phosphate of magnesia, and silicate of potash. In the straw which has served as litter, we add a further quantity of silicate of potash and phosphates; which, if the straw be putrified, are in exactly the same condition in which they were before being assimilated.

"It is evident, therefore, that the soil of a field will alter but little, if we collect and distribute the dung carefully; a certain portion of the phosphates, however, must be lost every year, being removed from the land with the corn and cattle, and this portion will accumulate in the neighborhood of large towns. The loss thus suffered must be compensated for in a well managed farm, and this is partly done by allowing the fields to lie in grass. In Germany, it is considered that for every 100 acres of corn-land, there must, in order to effect a profitable cultivation, be 20 acres of pasture-land, which produce annually, on an average, 500 lbs. of hay. Now, assuming that the ashes of the excrements of the animals fed with this hay amount to 6.82 per cent., then 341 lbs. of the silicate of lime and phosphates of magnesia and lime must be yielded by these excrements, and will in a certain measure compensate for the loss which the corn-land had sustained. The absolute loss in the salts of phosphoric acid, which are not again replaced, is spread over so great an extent of surface, that it scarcely deserves to be taken account of. But the loss of phosphates is again replaced in the pastures by the ashes of the wood used in our houses for fuel.

"We could keep our fields in a constant state of fertility by replacing every year as much as we remove from them in the form of produce; but an increase of fertility, and consequent increase of crop, can only be obtained when we add more to them than we take away. It will be found, that of two fields placed under conditions otherwise

similar, the one will be most fruitful upon which the plants are enabled to appropriate more easily and in greater abundance those contents of the soil which are essential to their growth and development" (pp. 181-2).

In attributing the fertilizing action of animal excreta to the silicate of potash and the phosphates of lime and magnesia LIEBIG differed from BOUSSINGAULT who laid the chief stress upon the more important element nitrogen. With regard to the use of bones as a fertilizer LIEBIG recommended a chemical treatment of great importance:—

"The primary sources from which the bones of animals are derived are the hay, straw, or other substances which they take as food. Now if we admit that bones contain 55 per cent. of the phosphates of lime and magnesia (BERZELIUS) and that hay contains as much of them as wheatstraw, it will follow that 8 lbs. of bones contain as much phosphate of lime as 1000 lbs. of hay or wheat-straw, and 20* lbs. of it as much as 1000 lbs. of the grain of wheat or oats. These numbers express pretty exactly the quantity of phosphates which a soil yields annually on the growth of hay and corn. Now the manure of an acre of land with 40 lbs. of bone dust is sufficient to supply three crops of wheat, clover, potatoes, turnips, &c., with phosphates. But the form in which they are restored to a soil does not appear to be a matter of indifference. For the more finely the bones are reduced to powder, and the more intimately they are mixed with the soil, the more easily are they assimilated. The most easy and practical mode of effecting their division is to pour over the bones, in a state of fine powder, half of their weight of sulphuric acid diluted with three or four parts of water, and after they have been digested for some time, to add one hundred parts of water, and sprinkle this mixture over the field before the plough. In a few seconds, the free acids unite with the bases contained in the earth, and a neutral salt is formed in a very fine state of division. Experiments instituted on a soil formed from grauwacke, for the purpose of ascertaining the action of manure thus prepared, have distinctly shown that neither corn, nor kitchen-garden plants, suffer injurious effects in consequence, but that on the contrary they thrive with much more vigour" (pp. 184-5).

The suggestion of LIEBIG to treat bones with sulfuric acid, in order to increase the availability of the phosphoric acid which they contained, marked the inception of the manufacture of phosphatic fertilizers, which has now become one of the world's leading chemical industries. ESCHER had previously announced in 1835 that finely ground bones, when digested with acid, had a more pronounced effect on increasing plant-growth than had untreated bone meal. LIEBIG apparently was not aware of ESCHER's prior suggestion (PACKARD 1937).

In the early stages of his mineral manure experiments LIEBIG held that the potash and other water-soluble salts of his fertilizer mixtures, in order to prevent their being leached away by rain, must first be converted by fusion with silicates into more insoluble forms. These glass-like combinations, even though finely ground, proved to be inert when applied to crops and LIEBIG's new mineral fertilizers began to encounter considerable opposition. Fortunately the discovery by WAY in 1850 of the natural absorptive power of soils for the soluble salts of potash and other bases caused LIEBIG to realize the mistake which he had committed. With the employment of

* Incorrectly printed "2" in PLAYFAIR's edition. LIEBIG's calculations here, as in other cases, are very faulty because of highly inaccurate analytical data. According to estimates based on later more reliable analyses given in KÖNIG's "Menschliche Nahrung und Genussmittel" and in WOLFF's "Aschen-Analysen", 17.6 lbs. of dried bone contain as much phosphoric acid as 1000 lbs. of meadow hay, 9.5 lbs. as much as 1000 lbs. of wheat straw, and 33.8 lbs. as much as 1000 lbs. of wheat grain.

these salts in their natural soluble form the expected response of crops to his fertilizers was immediately obtained.

The mineral theory of fertilizers has often been mentioned as LIEBIG's great contribution to agriculture, but since the necessity of supplying mineral elements to plants had previously been indicated by SPRENGEL and other writers, the claim of LIEBIG's priority here, as in the overthrow of the humus conception, has seemed open to question. AUGUST VOGEL (1874*b*), a pupil and eulogist of LIEBIG, has thus analyzed the situation:—

"As high as we may estimate in this respect the investigations of his predecessors, DE SAUSSURE, SPRENGEL, etc., and as much as we may recognize that efforts had been made before LIEBIG to demonstrate the importance of the inorganic constituents of the soil for the nutrition of plants in general and of individual elements for the different kinds of crops and for the different organs of plants, the fact nevertheless remains that LIEBIG was the first who recognized correctly the intimate relationship of plant ashes to the mineral constituents of the soil and proclaimed this with forceful energy and most firm resolution."

LIEBIG, by means of the reliable methods of ash analysis devised in his laboratory by WILL and FRESSENIUS, came to have a much more accurate knowledge of the composition of the mineral matter of crops than was possessed by DE SAUSSURE, or SPRENGEL. The latter had, however, long before LIEBIG, a full realization of the essentiality of the mineral matter of soils and fertilizers, and of the relative unessentiality of humus, to the growth of crops. It was LIEBIG's great contribution to demonstrate more convincingly than his predecessors the accuracy of this conception and to proclaim it more decisively by the force of his energetic propaganda. His most serious mistake was the failure to recognize at the same time the many indirect benefits of the organic matter in plant and animal manures.

In his discussion of the chemistry of cultivation LIEBIG advanced opinions which were also novel and stimulating. The main benefit of ploughing he ascribed to the increased oxidation of the organic matter of the soil by the entrance of air.

"In a soil to which the air has no access, or at most but very little, the remains of animals and vegetables do not decay, for they can only do so when freely supplied with oxygen; but they undergo putrefaction, for which air is present in sufficient quantity. Putrefaction is known to be a most powerful deoxidising process, the influence of which extends to all surrounding bodies, even to the roots and the plants themselves. All substances from which oxygen can be extracted yield it to putrefying bodies; yellow oxide of iron passes into the state of black oxide, sulphate of iron into sulphuret of iron, &c.

"The frequent renewal of air by ploughing, and the preparation of the soil, especially its contact with alkaline metallic oxides, the ashes of brown coal, burnt lime or limestone, change the putrefaction of its organic constituents into a pure process of oxidation; and from the moment at which all the organic matter existing in a soil enters into a state of oxidation or decay, its fertility is increased. The oxygen is no longer employed for the conversion of the brown soluble matter into the insoluble coal of humus, but serves for the formation of carbonic acid. This change takes place very slowly, and, in some instances, the oxygen is completely excluded by it. And, whenever this happens, the soil loses its fertility" (pp. 120-1).

In explaining the beneficial effects of crop rotation and fallowing LIEBIG adopted the root excretion theory of DE CANDOLLE and of MACAIRE-PRINSEP whose views he further elaborated as follows:—

"The quickness with which this decay of the excrements of plants proceeds, depends on the composition of the soil, and on its greater or less porosity. It will take place very quickly in a calcareous soil; for the power of organic excrements to attract oxygen and to putrify, is increased by contact with the alkaline constituents, and by the general porous nature of such kinds of soil, which freely permit the access of air. But it requires a longer time in heavy soils consisting of loam or clay.

"The same plants can be cultivated with advantage on one soil after the second year, but in others not until the fifth or ninth, merely on account of the change and destruction of the excrements which have an injurious influence on the plants being completed in the one, in the second year; in the others not until the ninth.

"In some neighbourhoods, clover will not thrive till the sixth year; in others not till the twelfth; flax in the second or third year. All this depends on the chemical nature of the soil; for it has been found by experience, that in those districts where the intervals at which the same plants can be cultivated with advantage, are very long, the time cannot be shortened even by the use of the most powerful manures. The destruction of the peculiar excrements of one crop must have taken place before a new crop can be produced.

"Flax, peas, clover, and even potatoes, are plants the excrements of which, in argillaceous soils, require the longest time for their conversion into humus; but it is evident, that the use of alkalies and burnt lime, or even small quantities of ashes which have not been lixiviated, must enable a soil to permit the cultivation of the same plants in a much shorter time.

"A soil lying fallow owes its earlier fertility, in part, to the destruction or conversion into humus of the excrements contained in it, which is effected during the fallow season, at the same time that the land is exposed to a further disintegration" (pp. 167-9).

The chemical transformation of the organic substances of plants and animals, as a result of fermentation, putrefaction and decay, constitutes the second part of LIEBIG's book upon the application of organic chemistry to agriculture and physiology. This subject forms a natural continuance of his general discussion of the cycle of elements in the operations of agriculture.

As in the case of his views concerning humus and mineral fertilizers, LIEBIG's opinions about fermentation caused him to become involved in another series of unfortunate polemical discussions. His theory of fermentation, very similar to that of STAHL, is briefly summarized in the statement that "a body in the act of combination or decomposition enables another body, with which it is in contact, to enter into the same state." This action is "ascribed to a new power termed the *catalytic force*" of which he mentions several chemical analogies.

"Platinum, for example, does not decompose nitric acid; it may be boiled with this acid without being oxidised by it, even when in a state of such fine division, that it no longer reflects light (black spongy platinum). But an alloy of silver and platinum dissolves with great ease in nitric acid; the oxidation which the silver suffers, causes the platinum to submit to the same change; or, in other words, the latter body from its contact with the oxidizing silver, acquires the property of decomposing nitric acid" (pp. 220-1).

According to LIEBIG the atoms of fermentable substances, such as sugar, are held together in a mere state of passivity by a certain *vis inertiae* of their elements (p. 227). When such a body comes in contact with a substance in an active state of decomposition, of which he took yeast as an example, the *vis inertiae* of its elements was destroyed by the mechanical motion of the vibrating yeast particles and new atomic arrangements were produced with the formation of alcohol and carbon dioxide. LIEBIG pointed

out that substances containing nitrogen, such as fulminate of silver and iodide of nitrogen, were particularly prone to have the balance of their elements upset. The same law held true in the organic world.

"Several bodies appear to enter spontaneously into the states of fermentation and putrefaction, particularly such as contain nitrogen or azotised substances. Now, it is very remarkable, that very small quantities of these substances, in a state of fermentation or putrefaction, possess the power of causing unlimited quantities of similar matters to pass into the same state. Thus, a small quantity of the juice of grapes in the act of fermentation, added to a large quantity of the same fluid, which does not ferment, induces the state of fermentation in the whole mass. So likewise the most minute portion of milk, paste, juice of the beet-root, flesh, or blood, in the state of putrefaction, causes fresh milk, paste, juice of the beet-root, flesh, or blood, to pass into the same condition when in contact with them" (p. 231).

The action of micro-organisms in decompositions of this kind was wholly unknown, when LIEBIG wrote this passage, and his explanation of the regeneration of yeast in fermenting liquids led him into strange speculations, as for example:—

"Yeast is a product of the decomposition of gluten; but it passes into a second stage of decomposition when in contact with water. On account of its being in this state of further change, yeast excites fermentation in a fresh solution of sugar, and if this second saccharine fluid should contain gluten, (should it be *wort*, for example,) yeast is again generated in consequence of the transposition of the elements of the sugar exciting a similar change in this gluten.

"After this explanation, the idea that yeast reproduces itself as seeds reproduce seeds, cannot for a moment be entertained" (p. 345).

Air and water, according to LIEBIG, were necessary for the activation of yeast and the preservation of fruit juices, meat, and vegetables by heating (*i.e.*, sterilization) he attributed to the exclusion of oxygen.

"Animal food of every kind, and even the most delicate vegetables, may be preserved unchanged if heated to the temperature of boiling water in vessels from which the air is completely excluded. Food thus prepared has been kept for fifteen years, and upon opening the vessels after this long time, has been found as fresh and well flavoured as when originally placed in them.

"The action of the oxygen in these processes of decomposition is very simple; it excites changes in the composition of the azotised matters dissolved in the juices;—the mode of combination of the elements of those matters undergoes a disturbance and change in consequence of their contact with oxygen. The oxygen acts here in a similar manner to the friction or motion which effects the mutual decomposition of two salts, the crystallisation of salts from their solution, or the explosion of fulminating mercury. It causes the state of rest to be converted into a state of motion.

"When this condition of intestine motion is once excited, the presence of oxygen is no longer necessary. The smallest particle of an azotised body in this act of decomposition exercises an influence upon the particles in contact with it, and the state of motion is thus propagated through the substance. The air may now be completely excluded, but the fermentation or putrefaction proceeds uninterruptedly to its completion. It has been remarked that the mere contact of carbonic acid is sufficient to produce fermentation in the juices of several fruits" (pp. 272-3).

We know now, as a result of the discoveries of PASTEUR, that the preservation of foods by heating in closed vessels is due not to the removal of oxygen as LIEBIG supposed but to the destruction and exclusion of micro-organisms.

LIEBIG's explanation of putrefaction was similar to his theory of fermentation. An internal combustion or oxidation analogous to dry distilla-

tion was assumed in both cases, the only difference being that in fermentation but one compound, such as sugar, was involved, whereas in putrefaction a number of substances were decomposed.

"We may now compare fermentation and putrefaction with the decomposition which organic compounds suffer under the influence of a high temperature. Dry distillation would appear to be a process of combustion or oxidation going on in the interior of a substance, in which a part of the carbon unites with all or part of the oxygen of the compound, while other new compounds containing a large proportion of hydrogen are necessarily produced. Fermentation may be considered as a process of combustion or oxidation of a similar kind, taking place in a liquid between the elements of the same matter, at a very slightly elevated temperature; and putrefaction as a process of oxidation, in which the oxygen of all the substances present comes into play" (pp. 259-60).

Decay, according to LIEBIG, differed from fermentation and putrefaction in being a slower exterior oxidation process.

"In organic nature, besides the processes of decomposition named fermentation and putrefaction, another and not less striking class of changes occur, which bodies suffer from the influence of the air. This is the act of gradual combination of the combustible elements of a body with the oxygen of the air; a slow combustion or oxidation, to which we shall apply the term of *eremacausis*.

"The conversion of wood into humus, the formation of acetic acid out of alcohol, nitrification, and numerous other processes, are of this nature. Vegetable juices of every kind, parts of animal and vegetable substances, moist sawdust, blood, &c., cannot be exposed to the air, without suffering immediately a progressive change of colour and properties, during which oxygen is absorbed. These changes do not take place when water is excluded, or when the substances are exposed to the temperature of 32°, and it has been observed that different bodies require different degrees of heat, in order to effect the absorption of oxygen, and, consequently their *eremacausis*. The property of suffering this change is possessed in the highest degree by substances which contain nitrogen" (p. 260).

In the final part of his book LIEBIG extended his mechanical theory of fermentation and putrefaction to the explanation of contagions, miasms and infections, but as these subjects fall outside the province of agricultural chemistry a consideration of them is not pertinent to our discussion.

LIEBIG'S "Organic Chemistry in its Applications to Agriculture and Physiology" was followed in 1842 by the companion volume of his contribution to the British Association upon the applications of organic chemistry. This was his "Animal Chemistry or Chemistry in its Applications to Physiology and Pathology," which was edited from LIEBIG'S manuscript by WILLIAM GREGORY, and was an extension of his former work to the fields of animal and human physiology. In the four years following its publication 12 editions and translations of the Animal Chemistry appeared—3 in Germany, 3 in America, 2 in England, and 1 each in France, Holland, Poland and Spain. Publication was discontinued in 1846.

Because of the lack of international copyright regulations, GREGORY'S London edition of LIEBIG'S "Animal Chemistry" was reprinted in the United States almost simultaneously at Cambridge, New York and Philadelphia, with bitter recriminations by the rival publishers. The Preface and Appendix in the Cambridge edition reflect the animosities of the incident. It is to Gregory's original London edition that the following citations and references pertain unless otherwise stated.

Many investigations in the field of animal chemistry had been made before LIEBIG took the field. CHEVREUL had published his classic researches

on the composition of animal fats in 1823, BERZELIUS had investigated the composition of urine, blood and bile, TIEDMANN and GMELIN had made a study of digestion and MULDER had started work on the proteins but no one had as yet attempted to effect a synthesis of these scattered researches until LIEBIG attempted to do for animal physiology what he had just tried to accomplish for agriculture. As LIEBIG's pupil A. W. HOFMANN (1875) remarked in his Faraday Lecture: —

"No one had ever ventured to collect these scattered efforts into a focus for the general elucidation of the phenomena of animal life. It was reserved for Liebig to accomplish this arduous task. Amidst the complex and apparently entangled phenomena attending the development and maintenance of animal vitality, Liebig was the first to discern and elucidate the precise and determinate action of chemical and physical laws."

As with the Agricultural Chemistry LIEBIG's ideas underwent so rapid a reconstruction with advancing knowledge that a comparison of later with earlier editions of his Animal Chemistry shows many omissions and differences of statement. In a significant passage contained in all editions of his Animal Chemistry LIEBIG wrote: —

"The cultivation of our crops had ultimately no other object than the production of a maximum of those substances which are adapted for assimilation and respiration, in the smallest possible space. Grain and other nutritious vegetables yield us, not only in starch, sugar, and gum, the carbon which protects our organs from the action of oxygen, and produces in the organism the heat which is essential to life, but also in the form of vegetable fibrine, albumen, and caseine, our blood, from which the other parts of our body are developed.

"Man, when confined to animal food, respire, like the carnivora, at the expense of the matters produced by the metamorphosis of organized tissues; and, just as the lion, tiger, hyaena, in the cages of a menagerie, are compelled to accelerate the waste of the organized tissues by incessant motion, in order to furnish the matter necessary for respiration, so, the savage, for the very same object, is forced to make the most laborious exertions, and go through a vast amount of muscular exercise. He is compelled to consume force merely in order to supply matter for respiration.

"Cultivation is the economy of force. Science teaches us the simplest means of obtaining the greatest effect with the smallest expenditure of power, and with given means to produce a maximum of force. The unprofitable exertion of power, the waste of force in agriculture, in other branches of industry, in science, or in social economy, is characteristic of the savage state, or of the want of cultivation" (pp. 77-8).

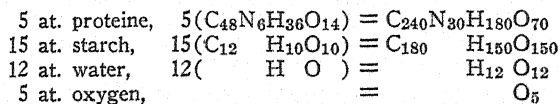
In his efforts to explain the transformations, which carbohydrates and proteins undergo in the animal organism in the presence of oxygen, LIEBIG gave free rein to speculation as is shown in the following passage (pp. 152-3): —

"If the elements of proteine and starch, oxygen and water being also present, undergo transformation together and mutually affect each other, we obtain, as the products of this metamorphosis, urea, choleic acid, ammonia, and carbonic acid, and besides these, no other product whatever.

The elements of

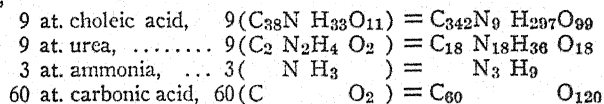
5 at. proteine	} = {	9 at. choleic acid
15 at. starch		9 at. urea
12 at. water		3 at. ammonia
5 at. oxygen		60 at. carbonic acid

In detail,—



The sum is = $\text{C}_{420}\text{N}_{30}\text{H}_{342}\text{O}_{237}$

and,—



The sum is = $\text{C}_{420}\text{N}_{30}\text{H}_{342}\text{O}_{237}$

This imaginary balance between the intake and outgo of the elements of food is a good illustration of the extravagant use which LIEBIG, MULDER and other chemists made of chemical formulas at the time of their first introduction. It was perhaps for fear that such speculations might be mistaken for established truths that LIEBIG omitted most of them in later editions of his "Animal Chemistry." In extenuating the employment of hypothetical formulas LIEBIG remarked: —

"I would constantly remind the reader, that their use is to serve as points of connection, which may enable us to acquire more accurate views as to the production and decomposition of those compounds which form the animal tissues. They are the first attempts to discover the path which we must follow in order to attain the object of our researches; and this object, the goal we strive to reach, is, and must be, attainable" (p. 143).

But while thus excusing his own conjectures LIEBIG had little patience with the use of similar speculations by others, as has been noted in his criticisms of MULDER's formulas for the hydrolysis of protein.

LIEBIG divided food into two classes, (1) the nitrogenous or plastic elements of nutrition which comprise vegetable fibrin, albumen and casein, animal flesh and blood, and (2) the non-nitrogenous or respiratory elements which comprise the fats, carbohydrates and alcoholic beverages (pp. 95-6). The foods of class (1) supply the body with the elements which are transported by the blood stream to form new growth and to restore the waste of muscle, cartilage, nerves, brain, and other cellular tissues, that have approximately the same elementary composition as the nitrogenous constituents of the food from which they were derived. The non-nitrogenous foods of class (2), when added to those of class (1), supply an excess of carbon and hydrogen that are consumed in the production of animal heat which, without this excess, would have to be supplied by the oxidation of the body's own tissues. The function of the carbohydrates and fats in reducing the losses of the body from destructive oxidation was especially stressed by LIEBIG (pp. 68-70).

In the muscular activities of the body there is a constant waste of nitrogenous tissues which is excreted from the system in the form of urea, uric acid, and other degradation products. LIEBIG announced that the nitrogen, carbon, hydrogen, sulfur, phosphorus, etc., of this urinary waste do not proceed directly from the food but only from the breakdown of the body's tissues which are being constantly replaced.

LIEBIG's classification of foods into the plastic and respiratory groups is not rigidly correct, for physiology now teaches that all organic foods during metabolism may yield respiratory products. The objections raised against his scheme did not affect, however, its general usefulness; as BISCHOFF (1874), the eminent German physiologist, remarked:—

"These objections, undoubtedly correct as they are of themselves, have not been able to supplant LIEBIG's main conception and they will never be able to do so for its truth as a whole will always remain. It renders, moreover, the everlasting service of pointing out to us in the shortest way the essential and unmistakable differences in foods."

LIEBIG was especially interested in the production of animal heat. Because of too low estimates for the calories produced by the combustion of hydrogen and carbon physiologists had been unable to obtain full agreement between the calories as calculated from the food metabolized and the calories actually produced by the experimental animal. The difference was attributed to other sources of heat than respiration. MAGENDIE (1844), the celebrated French physiologist, expressed the prevalent opinion of his time when he wrote in 1838:—

"According to DESPRETZ under the most favourable circumstances, and then only in herbivorous animals, respiration furnishes not more than 89 percentum of the animal heat, while in carnivorous animals it is not more than 80. Hence it is manifest that there are other sources of heat in the animal economy. They are probably connected with the processes of secretion, nutrition, and friction of the different parts on each other."

Explanations of this character did not satisfy LIEBIG who, after a careful revision of the subject in view of the latest most reliable figures for the combustion heats of carbon and hydrogen, declared it to be his established conviction that all of the measurable heat of an animal could be explained by chemical processes of combustion within the animal.

"The mutual action between the elements of the food and the oxygen conveyed by the circulation of the blood to every part of the body is THE SOURCE OF ANIMAL HEAT" (p. 17).

This opinion was more and more substantiated by subsequent experiments but it was not until 1891 that RUBNER by improved apparatus succeeded in obtaining an agreement between the results by direct and indirect calorimetry within a fraction of one percent.

LIEBIG also made calculations of the heat-producing or respiratory power of different foods. As LUSK (1922) remarks, his results are "a divination of RUBNER's subsequently enunciated isodynamic law."

	LIEBIG's respiratory values 1846	RUBNER's isodynamic values 1885
Fat	100	100
Starch	242	232
Cane-sugar	249	234
Dried meat	300	243

LIEBIG's announcement (pp. 82-8) that elaboration of fat can take place within the animal organism gave rise to a long controversy. It had previously been asserted by DUMAS and BOUSSINGAULT (1844) in their

"Essai de Statique chimique des Êtres organisés" that the fat, which the animal stores up, is derived as such from its vegetable food. Experiments proved that LIEBIG was correct in his statement. The amount of fat deposited in pigs and geese, that were fed exclusively on vegetable food, was greatly in excess of that contained in their rations.

While the theory of animal metabolism, as conceived by LIEBIG, was in the main correct he committed certain errors of detail, many of which, however, were eliminated in subsequent editions of his works. His failure, for example, to detect sugar in the blood caused him to repudiate the idea that sugar was taken into the circulation.

"The occurrence of sugar in the urine of those afflicted with *diabetes mellitus* (which sugar, according to the best observations, is derived from the food) coupled with its total absence in the blood of the same patients, obviously proves that starch and sugar are not, as such, taken into circulation" (pp. 167-8).

Another book of LIEBIG (1847), entitled "Researches on the Chemistry of Food," gives a further account of his work in animal chemistry. Section I of this book (pp. 1-28) deals with methods of investigation and contains an attack on MULDER's protein theory (see page 254 of this volume). Section II (pp. 28-121) gives an account of LIEBIG's important researches on creatine, creatinine, sarcosine, inosinic acid, lactic acid, and other water-soluble constituents (organic and inorganic) of the juice of flesh. LIEBIG's highly practical outlook is well illustrated in Section III (pp. 122-43) of his book, in which he discusses the economic cooking of meat, so as to avoid the loss in soluble phosphates and other extractives, that are frequently thrown out in the pot liquor, and the best methods of preparing soups. He also extols the restorative properties of meat extract which was first prepared in 1821 by PROUST who, with the collaboration of PARMENTIER, highly recommended it as a valuable stimulant in the diet. It was not, however, until after the publication of LIEBIG's "Researches on the Chemistry of Food" that the interest of the public was aroused in a product, which, under the name of "LIEBIG's Extract of Meat," became in subsequent decades an important article of commerce.

LIEBIG stressed particularly the value of the inorganic constituents of vegetable foods to animals and man; his mineral theory thus covered the entire range from soil and fertilizer to crop and from crop to man.

One of the great services rendered by LIEBIG was the publication of his memorable "Familiar Letters on Chemistry and its Relations to Commerce, Physiology and Agriculture" the first English edition of which was published at London in 1843. These letters owed their inception to a series of popular articles on chemistry which LIEBIG began sending to the *Augsburger Allgemeine Zeitung* in 1841. The immense favor with which these contributions were received caused LIEBIG in 1844 to assemble and publish them in book form: the work rapidly became the most popular and widely distributed of his works. It was by this book that LIEBIG's name became a household word in every country of the world. LIEBIG gave great attention to the revisions of this book, each new edition containing additional letters all written in his inimitable entertaining style. During his lifetime thirty different editions and translations of the "Familiar Letters on Chemistry" were published, 5 in Germany, 4 in France, 4 in Russia, 3 in Den-

mark, 3 in England, 3 in Italy, 3 in Spain, 2 in Holland, 2 in Poland, and 1 in Sweden. Other editions were published after LIEBIG's death. Because of this work of conveying to the general public accounts of the progress in chemistry at his laboratory and elsewhere LIEBIG has been called by SHENSTONE (1895) the earliest of extension teachers.

The sciences concerned with plant and animal life are greatly indebted to LIEBIG for his aid, as an experimental investigator, in helping to eliminate from scientific explanations all references to a mysterious energizing vital principle that operated independently of chemical and physical forces. Before LIEBIG's time vitalistic conceptions, such as the "archei" of PARACELSUS and VAN HELMONT, the "eau générative" of PALISSY, the "anima sensitiva" of STAHL, the "spiritus rector" of BOERHAAVE, the "transmuting power" of THAER and the "life atoms" of SPRENGEL, had been continually invoked when scientific explanations failed. The old prevailing doctrine that it was impossible to produce in the laboratory a chemical compound of plant, or animal, origin was disproved by WÖHLER's synthesis of urea in 1828 and with that historic event one of the great strongholds of vitalism was demolished. LIEBIG's powerful pen contributed to the overthrow of other long established mystical traditions, such as that of the spontaneous combustion of human beings, with the result that by his influence the standards of scientific writing in this respect were raised to a higher level.

LIEBIG's impulsive, combative nature and his unfortunate use of invective, involved him in a continual round of polemics with BERZELIUS, DUMAS, LAWES, MARCHAND, MEISSNER, MITSCHERLICH, MULDER, WOLFF, and others, who, taking advantage of the hasty erroneous statements in his writings, found many openings for renewed attacks. LIEBIG's impulsiveness, however, was only a manifestation of his wonderful zeal and enthusiasm. With this spirit he infused all the students who worked under him and without sparing himself, he spurred them on to great records of accomplishment.

Measured by the achievements of his graduates LIEBIG, without question, was the greatest chemistry teacher of all time. Among his famous pupils were FRESENIUS, HENNEBERG, HOFMANN, ERLÉNMEYER, KEKULÉ, KOPP, LOEW, PETTENKOFER and WILL, among Germans; GERHARDT and WURTZ, among Frenchmen; FRANKLAND, GILBERT, GLADSTONE, MUSPRATT, PLAYFAIR and WILLIAMSON, among Englishmen; and BREWER, WOLCOTT GIBBS, HORSFORD, JOHNSON, PORTER, LAWRENCE SMITH, and WETHERELL among Americans. It was largely LIEBIG's pupils who shaped the developments of organic, physiological and agricultural chemistry during the half-century that followed the closure of his school at Giessen.

The infusion of a new spirit in the study of science was perhaps LIEBIG's greatest accomplishment. ADOLF MAYER (1895), the most acute critic of modern agricultural chemistry, once remarked:—

"Even though the sharp tests of criticism should succeed in reducing to nothing all of the tangible accomplishments of LIEBIG in agricultural chemistry the moral significance of his influence can never be denied."

Perhaps the best account of this vitalizing influence of LIEBIG is that given by his American pupil Professor SAMUEL W. JOHNSON (1913):—

"It was in that spirit that Baron LIEBIG instructed the students who gathered in his laboratory from all quarters of the globe to learn the art of making discoveries in science. They were set to testing the truth of some idea or the correctness of some fact, or else to make new observations and discover new facts to lead to new ideas. It was not the novelty or the glory of discovery, but the genuineness of discovery that was regarded as of first importance. He listened patiently to their accounts of each day's progress, considered their plan of investigation, saw the apparatus or arrangements they devised, witnessed the observations they were led to, and heard the theories they imagined. He encouraged, but he criticized. He asked questions, suggested doubts, raised objections. His students were required not only to collect facts, or supposed facts, and to connect and complement them by comparison, analogies and theories but they were made to attack their theories in every weak point and to verify or disprove the supposed facts by scrutiny from every side."

Few great chemists have possessed to the same degree as LIEBIG the double endowment of discovery and exposition. The vigor of his statements, the aptness of his examples, the humor of his anecdotes, and the brilliance of his imagination, both in his lectures and in his books, were most effective in helping to secure a wide acceptance of the principles which he announced. More than any other investigator he indicated the directions in which the future course of agricultural chemistry was to proceed.

LIEBIG's productive Giessen period came to an end in 1852 upon his removal to the University of Munich to assume direction of its department of chemistry. Laboratory investigation now gave way to literary activity and the remainder of his life was spent in revising his books and in rounding out the details of his system of chemical philosophy.

The closing of LIEBIG's period at Giessen is selected as the terminus in this account of agricultural chemical origins. It marks on the one hand the summation of the influences which gave rise to the work of LIEBIG and on the other hand the beginning of the important influence which LIEBIG was to exercise, through his teaching and that of his pupils, on the subsequent history of agricultural chemistry.

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SUBJECT INDEX

- ACETIC ACID; LAVOISIER'S ANALYSIS 170
 Acetification, rôle of oxygen in 196
Agave americana, composition of fibre of 255
 "Aggregata" of Stahl 100
 "Agriculae fundamenta chemica" by Wal-
 terius and Gyllenberg 127-34, 256
 Agricultural analysis; Davy stresses importance
 206; improvements by Liebig 262-3, by Sau-
 sure 201, by Scheele 162; in Pliny's time
 16-8; methods of Hales 89-90, of Paracelsus
 25-6
 Agricultural chemical economics 250-1
 Agricultural chemical polemics; Ingen-Housz
 and Senebier 149-50, Liebig and Mulder 253-5,
 276, 279
 Agricultural Chemistry; an experimental science
 viii; Boussingault's interpretation 241-2;
 Boyle's contributions 54; Candolle's sugges-
 tions 217-9; Chaptal's treatment 184-8; Clay-
 ton's observations 81-4; Davy's views 205, 210;
 definitions of viii-x, 205, 210, 227; Duha-
 mel's work 113-6; Hales's views, 90-1; Hermb-
 städt's "Archiv" of 189-92; Home's opinion
 117-8; Lavoisier's investigations 176-7; Liebig's
 work 263-5; Palissy's views 29-32; Pliny's
 conceptions 10-8; relations to medicine 18, to
 plant physiology 211; Royal Society's interest
 61-2; Schübler's system 227-8; Sprengel's
 work 231-2
 Agricultural self-sufficiency 251
 Agricultural technology in ancient times 13-6
 Agricultural wastes; utilization as fertilizers 236
 Agriculture, defined viii; among Greeks and
 Romans 10
 Agronomy; Candolle's definition and divisions
 212; Schübler's subdivisions 228; Thae's dis-
 cussion 179-82
 "Agronomy, Agricultural Chemistry and Physi-
 ology" by Boussingault 251-2
 Air as plant food; Ingen-Housz's belief in 146-7;
 Tull's disbelief in 93-4
 Air as primal element; announcement of Anaxi-
 menes 1; Black destroys views of 135-7
 Air, composition of; work of Cavendish 154, of
 Priestley 141, of Rutherford 141, of Scheele
 158, of Senebier 151
 Alchemist of digestion 26-8
 Alchemy; view of Paracelsus 24, of Plantes 53
 Alcohol; analysis by Lavoisier 170, by Saussure
 202
 Aldehyde; discovery by Liebig 263
 Alkalies, potash and soda 113
 Alkaline base theory of Liebig 267-8, criticism
 of Sprengel 236, 268
 Amygdalin 263
 Analysis of plant ashes; Grew's attempts 77-8;
 Liebig's investigations 269, 271; Redi's table
 63; Saussure's work 200-1
 Analysis of plants; Hales's attempts 89-90
 "Anatome Plantarum" by Malpighi 73
 "Anatomy of Plants" by Grew 74
 "Anatomy of Vegetables begun" by Grew 73
Animal sensitiva of Stahl 104
 "Animal Chemistry" by Liebig 274-8
 Animal heat; investigations of Lavoisier 171-6,
 of Liebig 276-8
 Animal mucilage; Stahl's account 103
 Animal nutrition; Davy's discussion 206; Lavoisier's
 experiments 170-6; Liebig's work 275-8;
 relation of soils to 236
 "Annalen der Pharmazie" of Liebig 263
 "Annals of Agriculture" of Thae 179
 Antacid soil particles 120
 Apocrenic acid 255-8
 Archeus of digestion; of Helmont 44, of Para-
 celsus 26
 "Archidoxis" by Paracelsus 28
 "Archiv der Agriculturchemie" of Hermbstädt
 179, 189-90
 Argon; Cavendish's isolation 156
 Arsine discovered by Scheele 159
 Ash of plants; amounts removed per hectare 246;
 analyses by Saussure 200-2, by Sprengel 237-8,
 by Wiegmann 223-4; constituents of 215-6;
 dependent on soil 201-2; early work of Grew
 77-8, of Redi 62-5; importance of analyzing
 246, 269; need of restoring to land 268; not
 synthesized by plant 198-9, 210; varies in
 different plant-organs 201; views of Boyle 56,
 of Thae 181
 Asphyxiation in wineries 17
 Assimilation of hydrogen from water; views of
 Boussingault 244-5, of Liebig, 266
 Assimilation of nitrogen; Boussingault's work on
 243-4; Liebig's views 266-7
 Atomic Theory of Democritus 2-3; accepted by
 Boyle 54, by Grew 79, by Mayo 72; Aristotle's
 opposition 3-4; modern revival 3
 Azote (*see* Nitrogen)
- BACONIAN METHODS; "DRAGNET" CHARACTER 39;
 faults of 36
 Balanced crop and animal production 250-1
 Barley; ash percentages 223
 Barnyard manure; protection against losses 31,
 124, 210, 250
 Bechelbronn; Boussingault's farm experiments at
 239
 Beet sugar; Chaptal stimulates production 188;
 discovery by Marggraf 116-7
 Benzoic acid; isolated by Scheele 157; Wöhler
 and Liebig investigate 263
 Benzoyl radicle 263
 Blois; Lavoisier's farm experiments at 176-7
 Blood albumen; Mulder's formula for 254
 Bones; fertilizing action of 269-70; treatment
 with sulfuric acid 270
 Boyle's Law 62
 Bread; ancient processes 14
 Buckwheat; ash percentages 223
 Burnt clay as fertilizer 238
 Butter; ancient processes 15; unpleasant taste
 of 58
 Byproduct utilization; Glauber's methods 50
- CABBAGE; HALES' EXPERIMENT ON 88
Caesalpinia pluviosa 218
 Calcareous manures; Black's work on 137-8
 Calcination; Scheele's view of 158-9
 Calcium oxalate in plants; work of Scheele 162
 Caloric; Lavoisier's fire element 168
 Calorimetry; Lavoisier's experiments in 171-6
 Candle experiment; apparatus of Philo 6-7,
 158; Mayow's explanation 73; Priestley's em-
 ployment 143
 Carbon dioxide; assimilation by plants 146, 151,
 198, 245, 265; Black's investigations 135-7;
 cycle in nature, of Liebig 266, of Mulder 258;
 determination in soils 207; evolved by plants
 146; Helmont's discovery of 44-5; influence
 on plants 193-4, 197; internal plant origin of
 198; lime water test for 136-7; Priestley's
 work on 139; produced in germination 193
 Carbon monoxide; occurrence in submerged soils
 197
 Casein; Mulder's formula for 253
 Catalytic force 272
 Celle; Thae's farm experiments at 179
 Cereals; effect of fertilizers on yield and quality
 of 190-2
 Cheese; ancient processes for 15-16
 "Chemical Balance of Organic Nature" by
 Dumas and Boussingault 240-41
 Chemical equations 266
 "Chemical Researches on Plants" by Saussure
 192-204
 "Chemical Treatise on Air and Fire" by Scheele
 157, 161, 163
 Chemistry; apology for, by Boerhaave 110, by
 Liebig 265, by Senebier 150, by Sprengel 232;
 Lavoisier's true method of 170; Stahl's defi-
 nition 100
 "Chemistry applied to Agriculture" by Chaptal
 185-8; synopsis 186-7; technical treatment
 187-8
 "Chemistry for Farmers" by Sprengel 232
 "Chemistry of Tillable Soil" by Mulder 260;
 Bemmelen's review 260-1

- "Chemistry of Vegetable and Animal Physiology" by Mulder 253-60
 Chlorine; amount removed per hectare 246; discovered by Scheele 157; proved an element by Davy 205
 "Chymischer Glücks-Hafen" by Becher 98
 Citric acid isolated by Scheele 162
 Clover; ash percentages 223; assimilation of nitrogen by 244; elementary losses in germinating seeds of 242-3; influence of gypsum on ash of 247; mineral matter removed by per hectare 246
 Coagulation of milk; Boyle's explanation of 59
 Coal gas; first made by Clayton 82
 Combinations of matter; Aristotle's view of 4-5
 Combustion; explanation of Becher 97, of Heron 8, of Hooke 65-7, of Mayow 69-73, of Scheele 157-9, of Stahl 100; Lavoisier's investigations 168-74; relation to respiration 171-6; Royal Society's experiments on 61
Composita of Stahl 100
 Composition of crops; Boussingault's analyses 242-9; Davy's discussion 206-8; Einhof's analyses 182-3; Hermstädt's investigations 190
 Composting; experiments by Bacon 37-8, by Boussingault 249-50; Duhamel's view of 113-4; Glauber's method of 50; Liebig's discussion of 269
Conferua; evolution of oxygen and decomposition of carbon dioxide by 144-5
 Cooperative research; emphasized by Bacon 36; stimulated by Boyle 60-62
Corpora mixta of Becher 98
 Crenic acid 255-8
 Cultivation; chemistry of 271; Liebig on purpose of 275; Tull's theory of 92-5; Wallerius's view of 134
 Cupping-glass experiment of Heron 8-9
 DECAY; LIEBIG'S THEORY OF 274
 "De Ente Venini" by Paracelsus 26
 "De Re Metallica" by Agricola 34
 "De Separationibus Rerum Naturalium" by Paracelsus 25-6
 "De Tinctura Physicorum" by Paracelsus 24
 Digestion; Helmont's views of 44
 "Discours admirables" by Palissy 31
 "Discovery of Infinite Treasure" by Plattes 51-3
 Dry substance of plants; mostly derived from water and air 193
 Drying capacity of soils; Schübler's determinations 230
 Dung; effect of ration on composition of 249; elementary composition of 250; Tull disbelieves fertilizing action of 95
 EARTH AS PLANT FOOD; CONCEPT OF TULL 92-4; Duhamel's opinion 113; Wallerius opposes view of 130; Woodward's experiments on 85-6
 Egg albumen; Mulder's formula for 254
 Element; Boyle's definition of 54
 "Elementa Chymiae" by Boerhaave 105-6, 111
 Elements; losses of during germination 242-3; table of by Davy 205, by Lavoisier 167
 Elements essential to plants; list by Davy 205, by Sprengel 232-3
 "Elements of Agricultural Chemistry" by Davy 204-211
 "Elements of Agriculture" by Duhamel 113, 116
 "Elements of Chemistry" by Chaptal 184-6; popularity of 186; practical character of 184
 "Elements of Chemistry" by Lavoisier 164-73, 178
 Elements toxic to plants; list of Candolle 215, of Sprengel 236
 Emulsion 263
 Enclosed farms; effect of 51
 Eremacausis 274
 Erosion of soils; Plattes' views of 52-3
 "Essay on Food of Plants" by Ingen-Housz 147, 149
 Essential oils; methods of distilling 45-7
 Eudiometry; experiments of Cavendish 153-6, of Priestley 141, 144, of Senebier 151-2; improvements by Saussure 193, by Seguin 174-5
 Excreta; fertilizing action of 269-70
 Experimental farms; Boussingault's estate 239-40; Home's advocacy of 125-6; Lavoisier's farm 176-7
 Experimentation; "dragnet" method of Bacon 36-9, of Grew 74; emphasized by Boyle 54, 59, by Glauber 46, by Helmont 43-5, by Paracelsus 28; efforts of Home 119; field method of Boussingault 239; Hooke's facility in 68; in late Greek epoch 5-10; laboratory methods of Lavoisier 166, of Liebig 262-9, of Priestley 141-4, of Saussure 193, of Scheele 159-62
 "Experiments on Air" by Cavendish 153-7
 "Experiments and observations on different kinds of Air" by Priestley 140, 145
 "Experiments upon Vegetables" by Ingen-Housz 146, 149
Fagus sylvatica; OXYGEN ABSORPTION OF LEAVES 194
 Fallowing; views of Ingen-Housz 148, of Liebig 272, of Plattes 53
 "Familiar Letters on Chemistry" by Liebig 278-9, 281
 Farm experiment schools; Chaptal's advocacy of 188
 Fat formation by animals 277-8
 "Fatness of land" 38, 52
 "Fattening salt" of Glauber 48
 Fermentation; Boerhaave's view 109; defined by Sala 43, by Stahl 103-4; distinction from putrefaction 109-10; does not generate mineral matter 224; experiments of Hales 90, of Lavoisier 168-9; in presence and absence of oxygen 196; Liebig's theory of 272-3
 Fertilizers; classification of Davy 268, 210, of Sprengel 237; effect on growth and quality of crops 190-2; Liebig's calculation of requirements 268-9; views of Home 122, of Pliny 12-3, of Thaer 181-2, of Tull 95, of Wallerius 133-4; work of Boussingault 246-8, of Glauber 48-9, of Liebig 269-71
 Fibrin; Mulder's formula for 254
 Field experiments; of Boussingault 239-40, of Hermstädt 190-2, of Lavoisier 176-7, of Thaer 179
 Final causes; arguments from by Home 124, by Senebier 149
 Fire; explanation of Hooke 66-7, of Mayow 72, of Scheele 158-9, of Stahl 100
 Fire as primal element; ancient view of Heraclitus 1; belief in by Boerhaave 108, by Home 118, 123; Hooke's disbelief in 67; Lavoisier's "caloric" and "matière du feu" 168; Stahl's "phlogiston" 100-1
 "Fire air" of Scheele (oxygen) 158-9
 "Fixed air" (see Carbon dioxide)
 Flavors; Grew's explanation of 79
 Fleshy plants; exception of to Senebier's rule 198, 259
 Flour; ancient processes 13-14
 Foods; Liebig's classification of 276-7
 Forage crops; nutritive equivalents of 248
 "Foundations of Chemistry for Farmers" by Einhof and Thaer 179-183
 Four Elements Theory; ancient views of 1-8; accepted by Becher 97, by Boerhaave 108, by Grew 74, by Home 118, by Stahl 100, by Wallerius 129-30; opposed by Boyle 54
 Fume injury to plants; Candolle's discussion of 216, 219
 "Fundamenta Chymiae" by Stahl 98-100, 105
 "Fundamentals of Agricultural Chemistry" by Schübler 226-31
 GALLIC ACID ISOLATED BY SCHEELE 162
 "Gas"; word coined by Helmont 44
 "Gas sylvestre" (see Carbon dioxide)
 Gases; experiments with by Cavendish 153-6, by Hales 89-90, by Priestley 140-5
 Geic acid 255-8
 Gein 257
 "Generative water" of Palissy 32
 Germinating steep; Bacon's experiments 36-7; discussion of by Duhamel 114-5, by Sprengel 237, by Wallerius 133
 Germination; air needed for 67; elementary losses during 242-3; oxygen needed for 193
 Gluten; effect of fertilizers on yield of 192; first made by Duchesne 32; Mulder's formula for 253
 Glycerol isolated by Scheele 161
 Grape vine; Hales's experiments on 87-8

- Grasses; Davy's apparatus for studying 209; nutritive value of 206
 Greek laboratory apparatus 6, 9
 Green manuring; good and bad results of 215
 Gypsum; effect on ash of clover 247-8; Thae'r's recommendation of 182
- HEAT; PROMOTER OF PLANT GROWTH 129;
 Scheele's view of 159
 Heat retention of soils; Schübler's determination 230
 Homoiomeria; view of Anaxagoras 1-2, of Aristotle 2, 5, of Grew 74, 76
 "Horse-Hoeing Husbandry" by Tull 92-6
 Humic acid 255-7
 Humin 255-6
 Humus; decomposition products of 258; definition and description of 130-1, 196; destructive distillation of 196; fertilizing action of 234-5; importance of nitrogen of 246; properties of 197; rôle of in soil 258-9; Sprengel's analysis of 235
 Humus theory of plant nutrition; advocated by Davy 208-10, by Candolle 213, by Mulder 255-9, by Thae'r 180-1, by Wallerius 130-1; arguments for 256-8; opposed by Liebig 203, 257-9, 263, by Sprengel 234-5, by Wiegmann 225; qualified opinions of Boussingault 246, of Lavoisier 176, of Saussure 202-3
 "Hydraeleologia" by Sala 40
 Hydrogen; action of on plants 197; Cavendish's conversion of to water 154-5; named by Lavoisier 166
 Hydrogen of water; cycle of in nature 266; fixation by plants 244-5, 266
 Hydrogen sulfide discovered by Scheele 159
 Hydrolytic products of protein; Mulder's scheme 254
 Hygroscopicity of soils; Schübler's determinations 229
 Hypothetical formulas; use of by Lavoisier 169, by Liebig 275-6, by Mulder 254-5, 257, 260
- ITROCHEMISTRY; FOUNDED BY PARACELSUS 24
 Ice calorimeter of Lavoisier and Laplace 171-3
 Imbibition of water; Hales' experiments 88-9
 Imitations of nature; Grew's attempts 77
 Impediments of agriculture 124-5, 134
 Incubation of eggs; Réaumur's experiments on 112
 Inflammable airs; Priestley's work on 143
 "Inorganic Constituents of Plants" by Wiegmann and Polstorff 221-5
 Insecticide; wood tar as 49-50
 Isodynamic values of Rubner 277
- Jatropha brulans* 218
- LACTIC ACID ISOLATED BY SCHEELLE 159
 Latin; forsaken by Paracelsus 24
 Law of minimum; Sprengel's statement 233
 Leaves; apparatus for studying effect on air 195
 "Lectures on Elements of Chemistry" by Black 136, 138
Lepidium sativum (garden cress); ash content of seeds 224
 Life atoms of Sprengel 238
 Light as an element; views of Lavoisier 168, of Scheele 159, of Senebier 152
Lilium candidum; oxygen absorption of leaves 194
 Lime; amount removed by crops per hectare 246; views of by Thae'r 181-2, by Wallerius 131-2
 Lime-water test of Black 136-7
 Lixivial salts; Grew's determinations of 77-8
- MAGISTERIUM VINI OF PARACELSUS 28
 Magnesia; amount removed by crops per hectare 246
 Magnesia limestone; toxicity of to plants 138
 "Maize; Description, Culture and Use of" by Winthrop 80
 "Making Tar and Pitch" by Winthrop 80
 Malic acid isolated by Scheele 162
 Malt; making of, from maize 80-1
 Manures; care of 124, 210, 250; classification of by Home 122, by Sprengel 237; experiments on by Hermbstädt 191-2, by Lavoisier 177; hot and cold 52; spontaneous heating of 112; views of by Clayton 84, by Duhamel 113-4, by Glauber 48, by Palissy 30-1, by Plattes 52, by Thae'r 180-2, by Wallerius 133-4 (see also Fertilizers, Dung)
 Marl; account of by Pliny 13; Black's investigations 137-8; inquiry by Royal Society on 61; supposed heating effect of 31, 37; views of by Bacon 37, of Duhamel 113, of Home 122, of Palissy 31, of Thae'r 182, of Wallerius 132
 "Materia Medica" by Dioscorides 18-20
Materia prima, remota, media and proxima of Becher 97
Matière du feu of Lavoisier 168
 Maturation of fruits; Bacon's experiments 38-9; Boyle's explanation of 58
 Meat extract of Liebig 278
 Mechanistic philosophy of Grew 74-9
 Mephitic air (see Nitrogen)
 Metabolism; Boussingault's experiments 248-9; Lavoisier and Seguin's work 173-5; Liebig's investigations 275-8
 "Micrographia" by Hooke 65-7
 Mineral fertilizers; Boussingault's opinion of 247; discussion of by Davy 210, by Thae'r 181-2; Liebig's theory of 267-72; Sprengel's emphasis on 237
 Mineral matter; amounts removed by different crops per hectare 246-8; demands for by different crops 223-4, 235-6 by different plant organs 235-6; selective action of roots on 199; Wiegmann and Polstorff's proof of plant needs for 220-5
 "Mineral theory of manures" of Liebig 267-72
 Minerals injurious to plants; Candolle's list of 215-6; Sprengel's mention of 236
 Mint plants; evolution of oxygen by 143-4; growth in light and darkness 194
 "Mixta" of Stahl 100
 Möglin; Thae'r's Agricultural Institute at 179
 Molybdenic acid discovered by Scheele 159
Motus intestinus (internal motion) of Stahl; as cause of fermentation 103, 123; supposed transmuting action of 129
 Mucic acid prepared by Scheele 160
 Muck as fertilizer 84
 "Muck Manual" by Dana 256
- "NATURAL HISTORY" BY PLINY 10-17
 "New Atlantis" by Bacon 60
 "New Method of Chemistry" by Boerhaave 106-7, 111
 "New Philosophical Furnaces" by Glauber 45
 Nitrate formation; theory of Home 120-1, of Mulder 258
 Nitric oxide test for oxygen; discovery of by Priestley 141; use of by Cavendish 154, by Senebier 151-2
 Nitrogen; assimilation of by legumes 243-4; discovery by Rutherford 153, 156, 166, 170; fixation of by Cavendish 156; named Azote by Lavoisier 166; source of for crops 266-7
 Nitrogen fixation; Cavendish's experiment 156; supposed action of burnt clay 238, of humus 257-8
 Nomenclature; Lavoisier's reforms in 178
 "Novum Organum" by Bacon 34-6
 Nut-gall test 17
 Nutrition; Davy's study of grasses 206; views of Paracelsus 24-5, of Stahl 101
 "Nutrition of Plants" by Saussure 202-4
 Nutritive equivalents of forage crops; Boussingault's work 248, 263
- OATS; ASH PERCENTAGES 223; mineral matter removed by per hectare 246
 "Observables in Virginia" by Clayton 82-4
 "Observations on Lemon Juice" by Scheele 162
 "Occult food of life" of Wallerius 129
 "Oeuvres" by Lavoisier 165, 178
 Oil; ancient presses for 14-5; as a plant nutrient 118-9
 Oil of bitter almonds; investigated by Wöhler and Liebig 263
 "Oleaginous" meaning combustible 119
 Olive oil; elaidin reaction by Grew 77
 "On *magnesia alba*" by Black 135-139
 Organic analysis; Lavoisier's establishment of 170; Liebig's contributions to 262-3

- "Organic Chemistry in its Applications to Agriculture" by Liebig 263-75; popularity of 263-4; criticisms of 264-5
- Organic constituents of plants; Candolle's list of 216; production from carbonic acid and water 266
- "Ortus Medicinæ" by Helmont 43-5
- Oxalic acid formation; Mulder's theory of, 259
- Oxygen; determinations of in air by Cavendish 154, by Priestley 141, by Seguin 175, by Senebier 151; discovered by Priestley 139-41, 153, by Scheele 157; evolved by green plants 143-6, 151-2, 155, 198; influence of on grown plants 194-5; Lavoisier first sees significance of 166; named by Lavoisier 166; needed for germination 193; nitric oxide reaction of 141, 151-2; relation of to plant and animal life 143; rôle of in fermentation and decay 196
- Oxygen equivalent theory of Liebig 266, 268
- Oxygen formation by plants internally; Mayer's observations 198; Mulder's theory of 259
- "PALINGENESIS" DOCTRINE OF DUCHESNE 34
- Papyri manuscripts 18-19
- "Paramirum" by Paracelsus 27
- Peas; assimilation of nitrogen by 244
- Periwinkle plants; effect of on composition of air 194
- Pesca nigra* 219
- "Philosophic Dung" of Glauber 48
- Phlogiston theory; announced by Stahl 98-101; applications of 154; belief in by Cavendish 154-6, by Priestley 139-40, by Scheele 157-9, 163; Lavoisier's overthrow of 166-8
- Phosphoric acid; amount removed by crops per hectare 246; need of restoring to land 269-70
- Photosynthesis; facts of, found by Priestley 145; first explained by Senebier 149-52; formulas for reaction 57-8, 245, 260, 266; investigations of Boussingault 245; misinterpreted by Ingen-Housz 146, 148; views of by Cavendish 155, by Davy 206, by Candolle 213, by Mulder 259-60; by Saussure 193-5; with fleshy plants 198
- Physical methods; Davy stresses value of 211; developed chiefly by Schüller 225-30
- Plant antipathies; Home's theory of 125
- Plant components; list of by Candolle 216, by Davy 206, by Wallerius 128
- Plant diseases; Home's theory of 125
- Plant growth; maximum and minimum factors of 233
- "Plant humus, humic acid and its salts" by Sprengel 231-2, 239
- Plant juice movement; Hales' experiments on 86-8; view of Boerhaave 106-8, of Candolle 213
- Plant nutrition; early speculations 92; Priestley's phlogistic concept of 142; theory of Boerhaave 106, of Candolle 213, of Duhamel 115; views of Home 118, of Wallerius 128-9, of Liebig 267-8
- Plant organs; oxygen formation by 259-60; variation in mineral content of 235-6
- Plant physiology; Candolle's suggested researches in 217-9; influence on by Candolle 211-7, by Saussure 192-204; phlogistic explanation of by Cavendish 155, by Scheele 159; relations of to chemistry 211; view of Davy 206-8, of Grew 74-80
- "Plant Physiology" by Candolle 212-9
- Plant tissues; Mulder's investigations of 255
- Plant transmutation theory; belief in by Boyle 54-8, by Braconnot 215, by Ingen-Housz 146-8, by Schrader 215, by Thær 179-80; disproved by Saussure 198-9, by Wiegmann and Polstorff 221-5; opposed by Liebig 268, by Sprengel 231; persistence of belief in 220-1
- Plants; destructive distillation of 89; fixation of hydrogen by 244-5
- Plowing; increases oxidation of organic matter 271; Wallerius on need of 134
- Pneumatic trough; devised by Hooke 68
- "Pneumatics" by Heron 6-10
- Polygonum persicaria*; absorption of humus by 202
- Potash; amount of removed by crops per hectare 246; manufacture of in America 34
- Potatoes; mineral matter removed by per hectare 246
- Preservation of foods; ancient processes for 16
- "Principles of Agriculture and Vegetation" by Home 117-26, 128, 256
- "Principles of Fertilization" by Sprengel 232-7
- "Principles of Land Reclamations" by Sprengel 232-5
- "Principles of rational Husbandry" by Thær 179-83
- "Prosperity of Germany" by Glauber 48
- Protein; Mulder on composition of 253-5, on formation of 257
- Prussic acid discovered by Scheele 161
- Pumpkin experiment of Boyle 56
- Putrefaction; Boerhaave's experiments on 108-9; distinction from fermentation 109-10; Home's discussion of 123-4; Hooke's view of 68; rôle of oxygen in 196; theory of Stahl 123, of Liebig 272-4
- QUALITIES; DOCTRINE OF 4-5
- Quick lime; action of on soils 132; Black's work on 135-7
- RATIONS AND EXCRETA OF COW; ELEMENTARY BALANCE IN 249
- "Récepte véritable" by Palissy 29-31
- "Renovation of Soils" by Ingen-Housz 148-9
- "Researches on Chemistry of Food" by Liebig 278, 281
- "Researches on Influence of Solar Light" by Senebier 150, 152
- Respiration; experiments on by Lavoisier 170-6; Hooke's report on 68; Liebig's study of 277; relation of to combustion 171-6; Scheele's phlogistic conception of 159; view of Mayow 69-73, of Stahl 104-5
- Respiratory values of Liebig 277
- Root excretions; belief in by Boerhaave 106-8, by Candolle 213-5, 218, by Liebig 271-3, by Sprengel 236-7; Macaire's experiments on 214, 218, 224, 263; relations of to crop rotation 272; supposed toxicity of 213-5, 218, 236-7; Wiegmann's disproof of 224-5
- Root functions; assimilation of carbon dioxide 265; Candolle's views of 213; Ingen-Housz's views of 148; excretory organs 107-8, 213-5, 263, 271-2; selective absorption of mineral matter 198-200; supposed assimilation of humus 210, 213, 256
- Rotation of crops; relation of to root excretions 272; Thær's investigations on 179
- Royal Society; Boyle's relations with 60-1; Hooke's work as curator of 65-7; interest of in agricultural chemistry 61-2
- "Rural Economy" by Boussingault 241-52
- "SACCHAROLOGIA" by SALA 40-3
- "Sal Mirabile" (Glauber's salt) 46
- "Sal-nitre and nitro-aereal spirit" of Mayow 69
- Salsola kali* 113
- Saltpeter; Duchesne's view of 32; Glauber stresses value of 46; method of making by Bacon 37, by Glauber 48-9; theory of formation of Home 120-1, of Mayow 69-70, of Mulder 258; Tull's view of action of 94
- Salts as plant nutriment; view of Boyle 59, of Glauber 46, 48, of Home 120-1, of Palissy 30-1, of Paracelsus 24-5
- Salts as plant skeletons; view of Grew 75-6, of Home 122
- Saps; discussion of by Davy 208, by Duhamel 115; Hales's experiments on 86-8
- "Sceptical Chymist" by Boyle 54-6
- "Scheele's Green" 159
- Scholasticism; attacked by Bacon 34-6, by Glauber 46, by Helmont 43, by Paracelsus 22
- Seeds; changes of germinating 193; elementary losses in germinating 242; multiplicative power of 129
- Shrinkage of soils; Schüller's determinations 230
- Signatures; doctrine of 32
- Silica; amount of removed by crops per hectare 246
- Silicate of potash; recommended by Liebig as fertilizer 269-71
- Soda; Duhamel's discovery of 113
- Soil analyses; Boussingault questions value of 245-6; Sprengel's table of 234
- Soil deficiencies; Sprengel's determination of 233-4
- Soil exhaustion; effect of cropping on 199, 268; Ingen-Housz's explanation of 148

Soil physics; founded by Schübler 229-30
 "Soil Science" by Sprengel 232-5
 Soil sterility; root excretions as a cause of 213-5
 Soils; absorptive power for potash salts 270-1;
 Boyle's scheme for improving 59-60; classification of by Grew 74, by Sprengel 235, by Stahl 101-2, by Thaer 180; Davy's methods for analyzing 207-8; effect of on tobacco 82-4; Home's discussion of 120-2; mixing of 134; physical methods for studying 211, 229-30; relation of to animal nutrition 236; Royal Society's inquiries on 61; temperature measurements of Hales 88-9; views of by Paracelsus 25, by Pliny 10-12
Sophora japonica 218
 Specific gravity; introduced by Archimedes 18; Schübler's determinations of in soils 229
Sphaeria hypoxylon 219
Spiritus rector of Boerhaave 110
 "Spiritus sylvestris" (see Carbon dioxide)
 Spontaneous combustion; Boerhaave's explanation of 108-10; Clayton's view of 82; Duhamel's investigations of 116; Pliny's account of 16
 Starch; effort of urine and dung on yield of 192
 Sterilization of food; Liebig's oxygen-exclusion theory 273
 Stickiness of soils; Schübler's determinations of 230
 Sugar; analysis of by Lavoisier 170, by Sala 42; grades of 40; refining of 42; Stahl's account of 103
 Sulfuric acid; amount removed by crops per hectare 246; treatment of bones with 270
 "Sulphureous" meaning combustible; use of term by Clayton 82, Hooke 66-7, by Mayo 70-1
 Sunflower; Hales's experiment on 88
 Sunshine; plants evolve oxygen in 146
 "Sylvia Sylvarium" by Bacon 35-9
 Synthetic soil of Wiegmann 223
 TARTAR; ACCOUNT OF BY SALA 40, BY STAHL 103
 Tartaric acid isolated by Scheele 157
 "Tartarologia" by Sala 40
 Teaching agricultural chemistry; Liebig's pre-eminence in 279-80; Sprengel's courses 231
Telephora caerulea 219
Terra pinguis, mercurialis, and lapidia of Becher 97
 Thermometers; Hales's construction of 88-9; Réaumur's scale 112
 Three principles of Paracelsus 24-5; acceptance of by Glauber 46; Boyle's opposition to 54; qualified view of Bacon 36, of Becher 97, of Stahl 100

Tillage; Home's discussion of 121; views of Duhamel 113, of Liebig 271, of Tull 95
 Tobacco; ash percentages of 223; effect of soils on quality of 82-4
Tournefortia mutabilis 219
 Trace elements; Sprengel's statement 233
 Tungstic acid isolated by Scheele 160
 Turnips; amount of mineral matter removed by per hectare 246
 ULMIC ACID 255-8
 Ulmin; components of 255-6; conversion of wood into 255; relation of to humus 256-8
 Urea; synthesis of by Wöhler 279
 VEGETABLE COLORS; GREW'S WORK ON 78-9
 Vegetable gums; Stahl's account of 102-3
 "Vegetable Statics" by Hales 86-92
 Vetch; ash percentages of 223
 Vinegar; Liebig's study of 263; Scheele's method of preserving 160
 Virginia; early agriculture of 82-4; Liebig on depletion of soil of 268
 Vitalism; conceptions of Boerhaave 110, of Glauber 51, of Helmont 44, of Palissy 31-2, of Paracelsus 26-8, of Sprengel 238, of Stahl 104, of Thaer 179-81, of Wallerius 129-30; opposed by Liebig 279, by Saussure 198-9; persistence of belief in 220-1
 WATER; CAVENDISH'S DISCOVERY OF COMPOSITION OF 154-5
 Water as primal plant food; belief in by Becher 97, by Boyle 54-8, by Braconnot 147, by Helmont 43-5, by Thales 1, by Wallerius 130; disbelief in by Tull 94, by Woodward 84-6
 Waters; Clayton's examination of 82; Grew's classification of 74; Woodward's experiments on 85
 Wax formation from starch; Mulder's theory of 259
 Weeds; control of 125; injury of by theft of plant food 95, by toxic root excretions 214, 236-7
 Willow tree experiment of Helmont 44-5
 Wine; ancient processes for 14-15
 Wood; by-products from destructive distillation of 49-50
 Wood ashes; lixiviation of 33-4; use of in salt-peter making 49
 Wood charcoal 50
 YEAST; ACTIVATION OF BY AIR 273
 "Yliaster" of Paracelsus 22, 24
 "ZYMOTECNY" BY STAHL 103-5

AUTHOR INDEX

- | | | | |
|---|---|---|---|
| AGRICOLA, G., 33-4, 48 | Biringuccio, V., 48, 51 | 237, 248, 256, 264-5, 271 | Davy, J., 211 |
| Anaxagoras, 1-2, 5, 76 | Bischoff, T. L. W. von, 219, 277, 280 | Cato, 14 | Deischer, C. K., 51 |
| Anaximenes, 1, 147 | Black, J., 135-9, 152-3, 171 | Cavendish, H., 142, 152-6, 157-9, 163, 172 | Democritus, 2-3, 20, 54, 57-8, 72, 79, 108 |
| Archimedes, 18 | Block, A., 248 | Chambers, E., 106, 111 | Despretz, C. M., 277 |
| Aristotle, 1, 2-5, 20, 24, 34 | Blyth, A. W., 65 | Chaptal, J. A. C., 183-8, 229, 262 | Dingler, J. G., 220 |
| Armstrong, E. V., 51, 188 | Boerhaave, H., 31, 105-11, 122, 130, 213, 237, 279 | Chase, W. W., 116 | Dioscorides, 17-21 |
| Avicenna, 22, 24 | Bologna, J., 241 | Chevreur, M. E., 241, 274 | Dobbin, L., 73, 158-63 |
| Aykroyd, W. R., 178 | Bostock, J., 10, 21 | Chodat, F., 152 | Drachmann, A. G., 14-5, 21 |
| BACON, F., 3, 34-40, 43, 51, 59, 60, 72, 84, 92, 110, 132 | Boullay, P., 257 | Christison, R., 216 | Duchesse, J., 32-4, 122, 126 |
| Bay, J. C., 149, 152 | Boussingault, J. B., 126, 230, 239-52, 261, 263-4, 269-70, 277, 280 | Clark-Kennedy, A. E., 92 | Duhamel du Monceau, H. L., 112-16, 117, 130, 133, 147 |
| Becher, J. J., 97-8, 100, 119, 256 | Boyle, R., x, 3, 54-62, 65, 72, 84-5, 92, 111, 119, 130 | Clayton, J., 81-4, 135 | Dumas, J. A. B., 162-3, 240-1, 248, 252, 277, 279-80 |
| Beddoes, T., 161, 163, 204 | Braconnot, H., 147, 215, 221, 225, 241, 257 | Columella, 14, 15 | Dutrochet, R. J. H., 219 |
| Bemmelen, J. M. van, 235, 261 | Bradley, R., 93-4 | Crell, L. F. F. von, 160 | Einhof, H., 178-9, 182, 190, 205-6, 231 |
| Bergman, T., 126, 157, 159, 161, 163, 246 | Brewer, W. H., 279 | Cresciento, P., viii | Ellis, R. L., 40 |
| Berthelot, M., 178 | Brogliart, T., 241 | Cullen, W., 135 | Empedocles, 1, 6 |
| Berzelius, J. J., 131, 193, 203, 211, 220, 237, 257, 263-4, 275, 279-80 | Brown, A. C., 73, 138-9, 156 | Cuvier, G. L. C. F. D., 211 | Epicurus, 2 |
| Biot, J. B., 220 | Bulos, A., 210 | DANA, S. L., 256-7, 262 | Erdmann, O. L., 190, 220, 225, 232, 237-9 |
| Birch, T., 68 | CAJORI, F., 40 | Davis, T. L., 145 | Erlenmeyer, E., 279-80 |
| | Candolle, A. P. de, 108, 203, 211-19, | Davy, H., 138, 179, 182-3, 187-8, 203-11, 240-1, 256, 262, 264, 269 | Escher, 270 |

- FELLEBERG, P. E.
 von, 227
 Fludd, R., 7, 73
 Foster, M., 45, 105
 Foster, M. L., 32
 Frankland, E., 279
 Franklin, B., 116, 139
 French, S. J., 178
 Fresenius, C. R., 271, 279
 Fromberg, P. F. H., 253, 255, 262
 Fulton, J. F., 62
 GALEN, 18, 22, 24
 Gay-Lussac, J. L., 205, 262, 264
 Geoffroy, F. G., 113
 Gerhardt, C. F., 279
 Gibbs, O. W., 279
 Gilbert, J. H., 267, 279-80
 Gladstone, J. H., 279
 Glauber, J. R., 45-51, 60, 69, 92, 97, 132-3
 Gmelin, L., 275
 Gaudi, M. T., 51
 Graeger, N., 241
 Gregory, W., 274
 Grew, N., iii, 62, 73-80, 122
 Grimaux, E., 178
 Grimm, C., 260
 Gyllenberg, G. A., 127-8, 134
 HALE, S., 86-93, 135-6, 153, 211
 Hart, H., 204
 Harting, P., 255
 Hartmann, F., 29
 Hartog, P. J., 145, 178
 Harvey, H. M. W., 149
 Harvey, R. B., 149
 Heath, D. D., 40
 Hellriegel, H., 243-4
 Helmont, F. M. van, 43
 Helmont, J. B. van, 43-6, 51, 54, 56-7, 73, 84-86, 92-3, 98, 104, 130, 135-7, 147, 171, 198, 221, 279
 Henneberg, W., 279
 Heracitus, 1, 100, 147
 Hermbstädt, S. F., 179, 184, 189-92, 205
 Heron, 6-10, 21
 Hippocrates, 18
 Hofmann, A. W. von, 275, 279-80
 Home, F., 117-26, 128-31, 133, 256
 Hooke, R., 61, 65-9
 Hoover, H. C., 33
 Hoover, L. H., 33
 Horsford, E. N., 279
 Humboldt, A. von, 189, 262
 Huser, J., 22-9
 Hypatia, 18
 INGEN-HOUSZ, J., 145-50, 192-3, 206, 221
 JABLONSKI, P. E., 221, 223, 225
 Johnson, C. W., 183
 Johnson, S. W., viii, 279-80
 Johnston, J. F. W., 253, 262
 KASNER, K. W. G., 239, 262
 Keblor, L. F., 65
 Kekulé, F. A., 279
 Kendall, J., 163
 Kerr, R., 164-6, 169, 171, 178
 Knop, W., 138
 König, J., 270
 Kopp, H., 111, 279
 Kübel, J. A., 256
 Kunkel, J., 157
 LAGERCRANTZ, O., 19
 Lagrange, J. L., 164
 Lamarck, J. B. P. A. M., 211
 Lampadius, W. A., 202, 223, 225, 232, 237, 239
 Laplace, P. S., 171-2
 La Rive, A. D. de, 219
 Lavoisier, A. L., 10, 43, 71, 98, 125-6, 134, 139, 141, 145, 149, 152-3, 155-6, 159, 163-78, 183, 189, 192, 202, 204, 220, 241
 Law, G., 241, 251
 Lawes, J. B., 267, 279-80
 Lemery, L. H., 19
 Lemery, N., 113, 158
 Lemmermann, O., 225
 Lenglen, M., 252
 Lessaigne, J. L., 221, 223, 225
 Liebig, J. von, 5, 108, 110, 131, 150, 164, 183, 202-4, 214-5, 220, 231, 233, 235, 237, 239-40, 252-7, 258-9, 261-81, frontispiece
 Lippmann, E. O. von, 111
 Loew, O., 279
 Lones, T. E., 21
 Lucretius, 2-3
 Lukens, H. S., 188
 Lusk, G., 174, 178, 248, 252, 277, 281
 MACAIRE, also
 Macaire-Prinsep, J., 214, 216, 218-9, 224-5, 263, 271, 281
 Magendie, F., 277, 281
 Malpighi, M., 73
 Marchand, R. F., 279
 Marggraf, A. S., 113, 116-7, 120, 126, 163
 "Marvel, Ik." see Mitchell, D. G.
 Mather, C., 34
 Matthioli, P. A., 20
 Mayer, 182
 Mayer, A., ix, 198, 204, 259, 262, 279, 281
 Mayow, J., 67, 69-73, 89, 92-3, 100, 132, 170
 McKie, D., 178
 Meissner, P. T., 279
 Meldrum, A. M., 178
 Mesue, 24
 Meyer, E. von, 239
 Miller, F., 116
 Mills, J., 116, 134
 M'Intosh, J. G., 163
 Mitchell, D. G., viii
 Mitchell, S. L., 135
 Mitscherlich, E. E., 279
 Moleschott, J. A. W., 253
 Morris, G. S., 21
 Moulton, F. R., 281
 Müller, J., 260-1
 Mulder, G. J., 131, 203, 210, 241, 252-62, 276, 278-79
 Munro, H. A. J., 21
 Muspratt, J. S., 279
 NEUMANN, C., 157
 Newton, I., 3
 Norton, J. P., 253
 OESPER, R. E., 178
 Osborne, E. A., 280
 Oseen, C. W., 163
 PACKARD, W. G. T., 270, 281
 Packe, C., 46, 51
 Palissy, B., 29-32, 38, 47-8, 51-3, 110, 129, 132-3, 279
 Paracelsus, 21-29, 32, 34, 36, 38-9, 43-4, 46-7, 50-1, 60, 97-8, 103-4, 110, 128, 279
 Parmentier, A. A., 189, 278
 Parrot, 241
 Pasteur, L., 273
 Patterson, T. S., 73
 Petri, B., 248
 Pettenkofer, M. von, 279, 281
 Philo of Byzantium, 6-8, 73, 158
 Pilkinton, W., 134
 Plato, 1
 Plattes, G., 51-3
 Playfair, L., 263-4, 267, 270, 279
 Pliny (the elder), 10-18, 21, 31, 38, 243
 Polstorff, L., 220-5
 Porter, J. A., 279
 Porter, N., 21
 Priestley, J., 71, 139-147, 149, 151-5, 158, 163, 166, 175, 192, 206
 Pringle, J., 147
 Proust, J. L., 241, 278
 Puvis, M., 189
 QUERCETANUS, see Duchesne
 RAMSAY, W., 90, 92, 139, 156
 Rawley, W., 40
 Rayleigh, Lord (J. W. Strutt), 156
 Réaumur, R. A. F. de, 111-2, 137
 Redi, F., 62-5, 77-8
 Renwick, J., 189
 Riley, H. T., 10, 21
 Robinson, W. O., 197
 Robison, J., 138
 Rochas, H. de, 56
 Rouelle, G. F., 164
 Rubner, M., 277
 Rumford, Count (Benjamin Thompson), 204
 Rush, Benjamin, 135
 Russell, E. J., 215, 239, 252
 Rutherford, D., 141, 153, 156, 166, 170
 SACHSSE, R., 243
 Sala, A., 40-43, 103
 Saussure, H. B. de, 192
 Saussure, N. T. de, 64, 180, 183, 185, 189, 192-206, 210-1, 217, 220-1, 223-4, 231, 242, 244, 252, 259, 262, 264, 268, 271
 Schattenmann, 241, 250
 Scheele, C. W., 147, 154, 157-163, 168, 204
 Schmidt, W., 6, 8, 21
 Schrader, J. C., 180, 215, 221, 225, 232, 269
 Schreiner, O., 215
 Schübler, G. S., 180, 211, 225-31, 262, 264
 Seguin, A., 173-6
 Senebier, J., 149-152, 155, 192-3, 198, 204, 206, 241, 244, 259, 265
 Shaw, P., 57-9, 62, 105, 106-7, 111, 122
 Shaw, W., 183
 Shelburne, Lord (W. P. Fitzmaurice), 139
 Shenstone, W. A., 279, 281
 Shull, C. A., 96
 Smith, C. S., 51
 Smith, J. L., 279
 Spedding, J., 40
 Sprat, T., 61-2
 Sprengel, C., 108, 130, 179-80, 203, 215, 220, 223, 225, 230-9, 245, 257, 262-4, 268, 271, 279, 281
 Sprengel, K., 239
 Stahl, G. E., 43, 92, 98-105, 111, 119, 121-3, 126, 129, 139, 147, 154, 157, 159, 160, 163, 166, 168, 256, 272, 279
 Stillman, J. M., 29
 Stoddart, A. M., 29
 Sudhoff, K., 29
 Synesius, 18
 TENNANT, S., 138, 189
 Thaeer, A., 131, 178
 Thomsen, T., 256
 Thorpe, T. E., 145, 153-7
 Tiedmann, F., 275
 Tollens, B., viii
 Tull, J., 90-6, 112-3, 121, 130, 133, 147
 Turner, E., 216
 UEBERWEG, F., 21
 VAUQUELIN, L. N., 241, 256
 Virtanen, A. I., 50
 Vogel, A., 271, 281
 Volhard, J., 281
 Vries, H. de, 198, 204
 WAITE, A. E., 29
 Waksman, S. A., 262
 Wallerius, J. G., 119, 121, 124, 126-134, 162, 256
 Walsner, E., 224
 Way, J. T., 270
 Wellman, M., 21
 Wetherell, C. M., 279
 Whitney, M., 215
 Wiegmann, A. F., 220-25, 268
 Wiesner, J., 149
 Wilfarth, H., 244
 Will, H., 271, 279
 Williamson, A. W., 279
 Wilson, G., 157
 Winthrop, Jr., J., 49, 80-1
 Wöhler, F., 263, 279, 281
 Wolff, E. T., 235, 270, 279
 Woodward, J., 84-6, 92-3, 130
 Wurtz, C. A., 279
 ZEKERT, O., 163
 Ziegler, G. M., 32

Addendum

SOME REFERENCES TO THE HISTORY OF AGRICULTURAL CHEMISTRY IN THE CENTURY 1840-1940

The year 1940, which marked the centenary of the publication of LIEBIG's "Organic Chemistry in its Applications to Agriculture and Physiology," was the occasion of several anniversary historical publications dealing with some of the influences of LIEBIG's work on subsequent developments in agricultural chemistry. The influence of LIEBIG on the development of various branches of the fertilizer industry was discussed at a symposium of the Fertilizer Division of the American Chemical Society at Detroit on September 10, 1940, in a series of papers that were published in issues of the "American Fertilizer" from March 1 to May 10, 1941. The papers of another symposium devoted to LIEBIG's influences on subsequent developments in agricultural chemistry and in plant and animal physiology, held by Section C of the American Association for the Advancement of Science at Philadelphia in December 1940, were published in Monograph No. 16 of the Association under the title "LIEBIG and after LIEBIG."

An address by Prof. PAUL WALDEN of the University of Rostock entitled "Begründung der Agrikulturchemie durch JUSTUS LIEBIG in Jahre 1840" was published in "Forschungen und Fortschritte" for March 1941, pp. 98-100. An article "Hundert Jahre Agrikulturchemie" by Prof. K. SCHARER of the University of Giessen appeared in the "Chemiker Zeitung" for December 18, 1940, pp. 493-496. Another review "A Century of LIEBIG's Theory of Mineral Nutrition of Plants and of Soil Fertility" by B. VISWA NATH was published with a bibliography of 30 references in "Current Science" (British India) for December 1940, pp. 529-532. The most complete of these anniversary memorials of LIEBIG is a small book of 116 pages, entitled "Die Agrikulturchemie und ihre Bedeutung für die Volksernährung—Ein Rückblick und Ausblick" by Prof. OTTO LEMMERMANN of the University of Berlin (Braunschweig, Friedr. Vieweg und Sohn, 1940). It gives a brief sketch of agricultural chemistry from the earliest times to the present with special emphasis upon the work and influence of LIEBIG.

A complete general history of agricultural chemistry has not yet been written and for a broad picture of past developments in this field the student must piece together for himself the scattered references in biographies, histories of chemistry and text books of agricultural chemistry.

The history of chemistry, or of any of its periods or branches, such as ancient, medieval, organic, physical, physiological, agricultural, etc., can be treated in various ways. It can be presented biographically by giving accounts of the lives of those who have contributed to the advancement of the science. This method because of its appeal to non-professional readers is usually recommended to beginners for collateral reading in their introductory courses of study. Such readings of detached lives, however valuable for their human interest, do not always give a balanced view of the relationship of the individual to the scientific history of his period. This objection has been partially overcome by comparative biographies of selected men of science, as in WILHELM OSTWALD's "Grosse Männer" (Leipzig, Akademische Verlagsgesellschaft, 1909) which contains sketches of DAVY and LIEBIG that are interesting for the author's philosophic views of the mutual relationships of character, personality and genius, and as in PHILIPP LENARD's "Great Men of Science; A History of Scientific Progress" (translated from the second German edition by H. STAFFORD HATFIELD with a preface by E. N. DA C. ANDRADE. New York, The Macmillan Co., 1933) which gives short sketches of BOYLE, BLACK, SCHEEL, PRIESTLEY, CAVENDISH and DAVY, with interpretations of their life history and character.

The classification of chemical books according to author, edition, time and place of publication, constitutes another method of treating the history of chemistry. This method is best exemplified by HENRY C. BOLTON's "Bibliography of Chemistry" (Smithsonian Institution, 1893), a work invaluable to every chemical student and research worker, in which and in its two supplementary volumes (1899, 1904) are 258 references to books on agricultural chemistry. If BOLTON's monumental work could be brought up to date, the total number of books on agricultural chemistry would considerably exceed five hundred.

The history of science may also be presented by combining the biographic and bibliographic methods of treatment. This method is best illustrated by J. C. POGGENDORFF's twelve volume "Biographisch-Literarisches Handwörterbuch zur Geschichte der exacten Wissenschaften" (Leipzig, Johannes A. Barth, 1863-1904; Berlin, Verlag Chemie, 1925-1940). Brief biographic sketches and lists of the works of eminent contributors to the exact sciences from ancient times down to the year 1931 are given in the five editions of this most useful compilation.

A more specialized method of treating the history of chemistry is to trace the development of general principles, as has been done, for example, by M. M. PATTISON MUIR in his "History of Chemical Theories and Laws" (New York, John Wiley and Sons, 1907) and by A. LADENBURG in his "Vorträge über die Entwicklungsgeschichte der Chemie in den letzten 100 Jahren" (Zweite verbesserte und vermehrte Auflage, Braunschweig, 1887. English translation by LEONARD DOBBIN under the title "Lectures on the History of the Development of Chemistry since the Time of LAVOISIER," Edinburgh, The Alembic Club, 1900). In this method of treatment biographical references are largely omitted.

The history of chemistry has also been written from the viewpoint of its elements and compounds. This is the method followed by T. M. LOWRY in his "Historical Introduction to Chemistry" (London, Macmillan and Co., 1915). Lowry's history deals chiefly with the description and interpretation of classic experiments upon the solids, liquids and gases of chemistry, with no attention to chronological periods and with the transfer of biographic and bibliographic material to an appendix.

The student of the history of chemistry will find all of these various approaches to the subject helpful. The most satisfactory treatment is one that makes use of all these methods of presentation with careful observance of unity of composition, conservation of interest and exclusion of national bias. The nearest approach to this standard is the classic four volume "Geschichte der Chemie" of HERMANN KOPP (Braunschweig, Friedrich Vieweg und Sohn, 1843-1847) than which, for the period which it covers, no better or more complete work has yet been published. KOPP's outlook was broad. He showed the historic interrelations not only of the different branches of chemistry but of chemistry with other fields of science.

KOPP wrote his history while working as privat-docent in LIEBIG's laboratory at Giessen and thus was an eye-witness of the early growth-pains of agricultural chemistry. He recognized the significance of the investigations of SENEBIER, EINHOF, CHAPTAL, HERMBSTÄDT, DE SAUSSURE, DAVY, SCHÜBLER and other workers of the early nineteenth century (Vol. II, p. 137) as preparatory to a greater knowledge of the important relationships of chemistry to agriculture and devoted three pages of his history (Vol. I, pp. 434-7) to the important further contributions in this field by LIEBIG. He foresaw the future importance of agricultural chemistry but resigned the task of interpreting later developments in this field to a future historian. This was done 45 years later by ERNST VON MEYER in his "Geschichte der Chemie von den ältesten Zeiten bis zur Gegenwart, zugleich Einführung in das Studium der Chemie" (Leipzig, Veit und Comp., 1889). It was translated into English by GEORGE M'GOWAN under the title "A History of Chemistry from earliest Times to the present Day, being also an Introduction to the Study of the Science" (London, Macmillan and Co., 1891). This history of chemistry is less than one third the size of that by KOPP and as a condensed introduction to the subject necessarily lacks much of the detailed information given by the latter work; nevertheless VON MEYER devotes 16 pages of his book to historical developments in agricultural chemistry and in the related fields of physiological chemistry, plant chemistry, animal chemistry and the chemistry of fermentation and decay.

The best aids for gaining a knowledge of developments in agricultural chemistry during the last half-century are the historical references in the leading recent treatises upon soil science, agronomy, plant and animal physiology, dairying, conservation of crops and other branches of farm technology. Excellent historical introductions are found, for example, in E. J. RUSSELL's "Soil Conditions and Plant Growth" (seventh Ed.; London, Longmans, Green and Co., 1937); F. CZAPEK's three volume "Biochemie der Pflanzen" (dritte Auflage; Jena, Gustav Fischer, 1922-1925); F. LAFAR's five volume "Handbuch der Technischen Mykologie" (zweite Auflage; Jena, Gustav Fischer, 1904-1914); R. A. DUTCHER and D. E. HALEY's "Introduction to Agricultural Biochemistry" (New York, John Wiley and Sons, 1932); and E. KREMERS' "Introduc-

tion to Phytochemistry" (Bulletin of the Univ. of Wisconsin, Serial No. 1732, Madison, 1931). Special historical reviews of developments in the United States in "The Chemistry of Physiology and Nutrition" by GRAHAM LUSK and in "Agricultural Chemistry" by C. A. BROWNE are included in "A Half-Century of Chemistry in America 1876-1926. An historical Review commemorating the fiftieth Anniversary of the American Chemical Society" (EASTON, Amer. Chemical Soc., 1926).

An encouraging sign for the future growth of historical research in agricultural chemistry is the increasing amount of attention which the text books of this science devote to supplying students with references to original source material for collateral reading.